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VOLUME 11 Nos. 1/2

JANUARY/FEBRUARY 1957

PERGAMON PRESS LONDON · NEW YORK · PARIS

Geochim. et Cosmochim. Acta
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Publishing Offices: Pergamon Press Ltd., 4 & 5 Fitzroy Square, London W.1. (EUS 4455)

Subscription per volume (including postage) (A) £5 10s. (U.S.A. $15.40); (B) For individual subscribers certifying that the journal is for their private use, £3 10s. (U.S.A. $9.80)

Back numbers, £7 ($19.60) per volume

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PERGAMON PRESS, INC., 122 EAST 55TH STREET, NEW YORK 22, N.Y.
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Geochimica et Cosmochimica Acta, 1957, Vol. 11, pp. 1 to 27. Pergamon Press Ltd., London

Studies on the relative abundances of isotopes

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Department of Geology and Mineralogy, Oxford

(*Received* 15 *April* 1956)

Abstract—Trends and variations of relative abundance are apparent in general (all isotope species) N,Z isotope-abundance diagrams or charts. For critical study, different isotope species (even Z, even N; even Z, odd N and odd Z, even N) must be examined separately.

The most conspicuous feature about the even Z, even N species is a regular and profound relative abundance variation between $N = 30$ ($Z = 28$) and highly favoured $N = 50$. Though highly favoured $N = 82$ also strongly affects the relative abundances of even Z, even N isotopes, no comparable development precedes this neutron number. There is, however, a distinct relative abundance displacement at $Z = 52$ (tellurium) which appears to have significant consequences. Relative-abundance distribution and variations of even Z, odd N isotopes do not in general appear to be related to those involving even Z, even N species.

The relative abundances of isotopes of the thirteen odd Z elements with two (both even N) isotopes seem to vary closely with neutron excess. Three regularities may be distinguished. One which involves Rb—Sb—Re, the only odd Z elements with one isotope a neighbouring isobar, becomes linear when allowance is made for decay of Rb^{87} and Re^{187} over a period of $\sim 5000 \times 10^6$ years.

Principal isotopes of even Z–odd Z neighbouring elements tend to occur as isotonic pairs, often in quite well-defined sequences; these are interrupted at and immediately following $N = 20$, 50, and 82. The odd Z component of each such isotonic pair has the greater neutron excess up to $N = 34$, but the reverse holds after $N = 44$; this relationship is disturbed at and immediately following $N = 50$ and 82.

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INTRODUCTION

CLOSELY related to the problem of the variation of the cosmic abundances of the elements and individual nuclides is that of the variation of the relative abundances of isotopes; both depend on the mechanism(s) of formation of the elements and on nuclear structure. Unlike cosmic abundance data, which suffer from some uncertainty—because of the presence of analytical error and because of some doubt about the validity of the sources (meteorites, solar and stellar atmospheres) for estimating cosmic abundance—relative abundances of isotopes are accurately known from mass spectrometric measurements. Accordingly, they may be

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examined very critically for the presence of possible regularities and significant relationships.

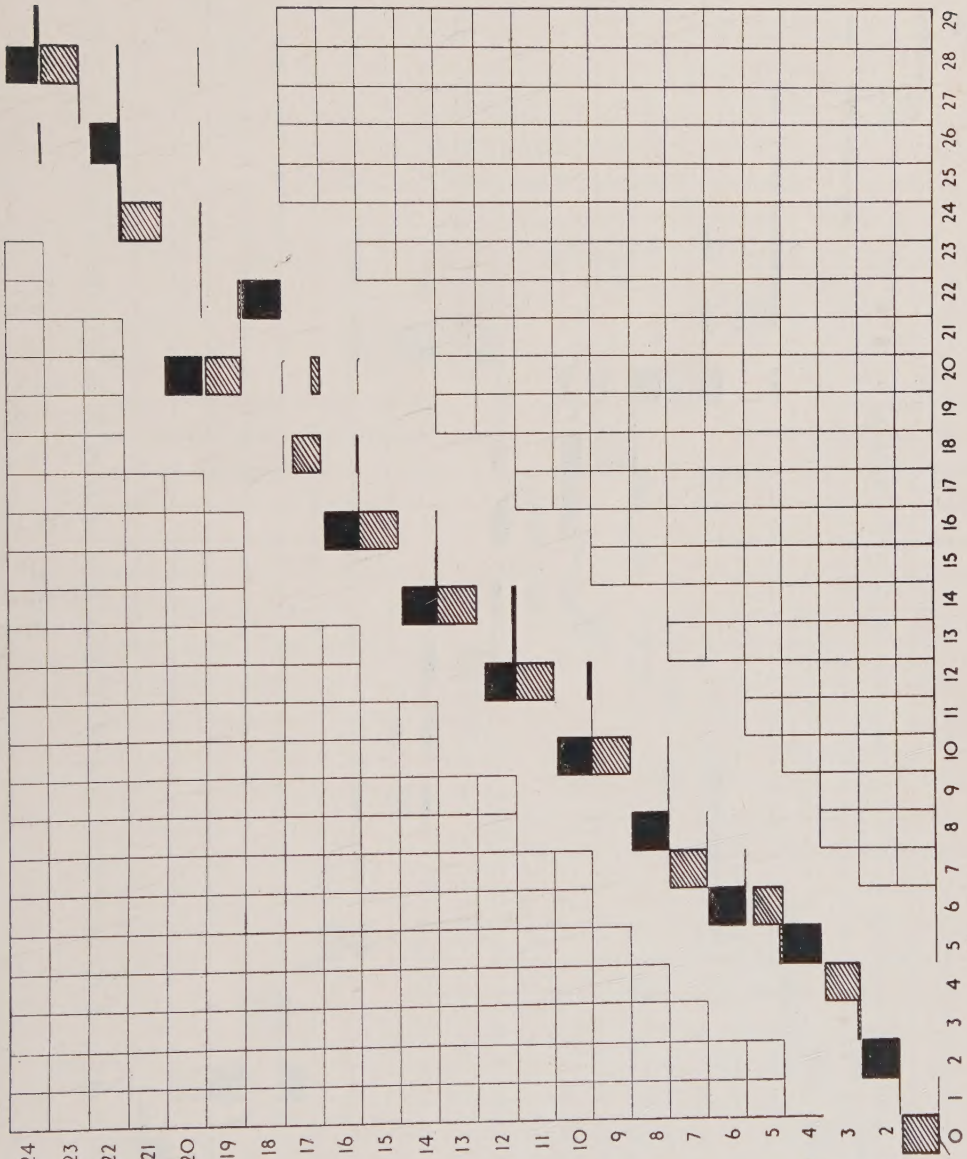
Relative abundance has not been emphasized in theories of the origin of the elements (for review, see Alpher and Herman, 1953; and literature survey, Rankama, 1954) or in theories of nuclear structure (for example, see Mayer and Jensen, 1955). Neither is it given prominence in studies of nuclide systematics, which tend to concentrate on *numbers* of isotopes, isotones, isobars and their relationships (see, for example, Feather, 1952). Lack of emphasis hitherto on relative abundance does not necessarily imply lack of significance, particularly if well-defined relationships are found to exist, and satisfactory theories of the origin of the elements and of nuclear structure must ultimately be able to account for them. Consideration of such regularities may in turn be helpful for gaining greater insight into the mechanism of formation of the elements and of nuclear structure. Accordingly, in these studies of the relative abundances of the isotopes, it will be our main task to seek and demonstrate a variety of relationships, some of which might be significant for the study of the origin of the elements, their abundances, and for theories of nuclear structure.

A general impression of isotope-abundance distribution and variation may be obtained from inspection of Figs. 1 to 4. These figures are N,Z diagrams* in which the height of a block indicates the per cent abundance of an isotope. Several well-known relative-abundance features are clear; for example, the greater relative abundances of the even N isotopes in the even Z elements, high relative abundances of even Z principal isotopes in the low Z and N range, significant developments in the region of highly favoured $N = 50$ and $N = 82$. Many other features are apparent or will become so, but for the purpose of further and closer study it will be more instructive to consider relative-abundance distribution and variation in each species group in turn, in the order, even Z, even N; even Z, odd N; and odd Z, even N. A discussion on principal isotopes follows, and finally a brief consideration of the extent to which various relative-abundance developments correlate with well established and other possible favoured or significant neutron numbers.

Relative Abundances of Even Z, Even N Isotopes

Fig. 5 is an N,Z relative-abundance diagram, similar to Figs. 1 to 4, but for even Z, even N isotopes only. Up to N and $Z = 20$, relative abundance follows a distribution which is characterized by the presence of one dominant principal light isotope in each element. The displacement at argon is exceptional. As measured now, A^{40} is the principal isotope of argon, but as the major proportion of terrestrial argon is evidently derived from electron-capture decay in K^{40} (see, for example, Rankama, 1954, for discussion and general literature survey), A^{36}, the next most abundant isotope of argon, was probably the most abundant argon isotope shortly after the elements were created. Following N and $Z = 20$, there is a short series of three elements, Ti, Cr, and Fe, each with one centrally disposed dominant principal isotope. The development which follows leading up to $N = 50$ (a highly favoured neutron number) and given in greater detail as Fig. 6, is the most

* Greater detail may be seen in larger isotope-abundance charts (Ahrens, 1956c).



Figs. 1–4. N, Z isotope abundance diagrams (all species). Height of block gives approximate indications of percentage. Black, even Z elements; diagonal lines, odd Z.

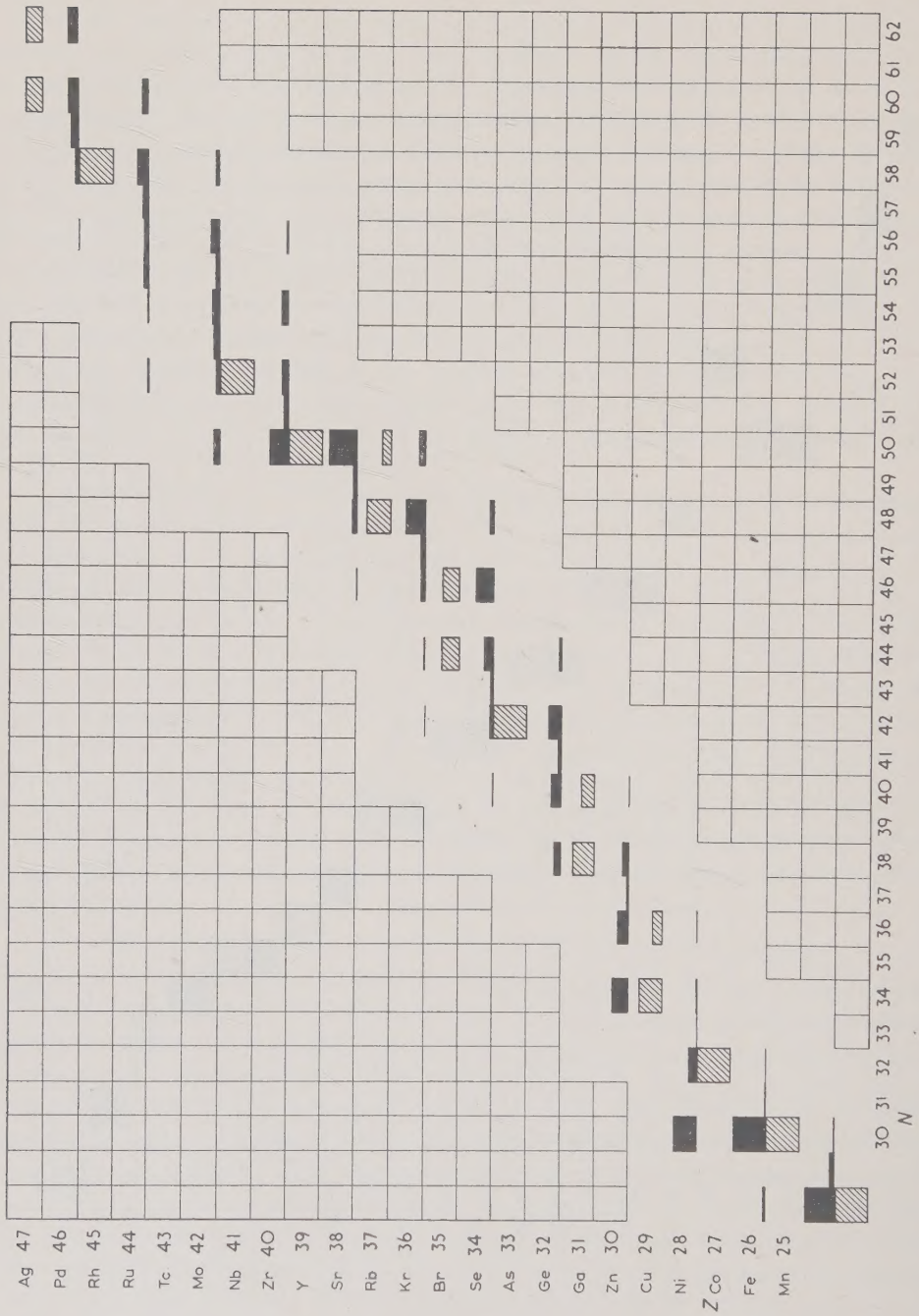

Ag 47
Pd 46
Rh 45
Ru 44
Tc 43
Mo 42
Nb 41
Zr 40
Y 39
Sr 38
Rb 37
Kr 36
Br 35
Se 34
As 33
Ge 32
Ga 31
Zn 30
Cu 29
Ni 28
Co 27
Fe 26
Mn 25
Z
30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62
N

Fig. 2

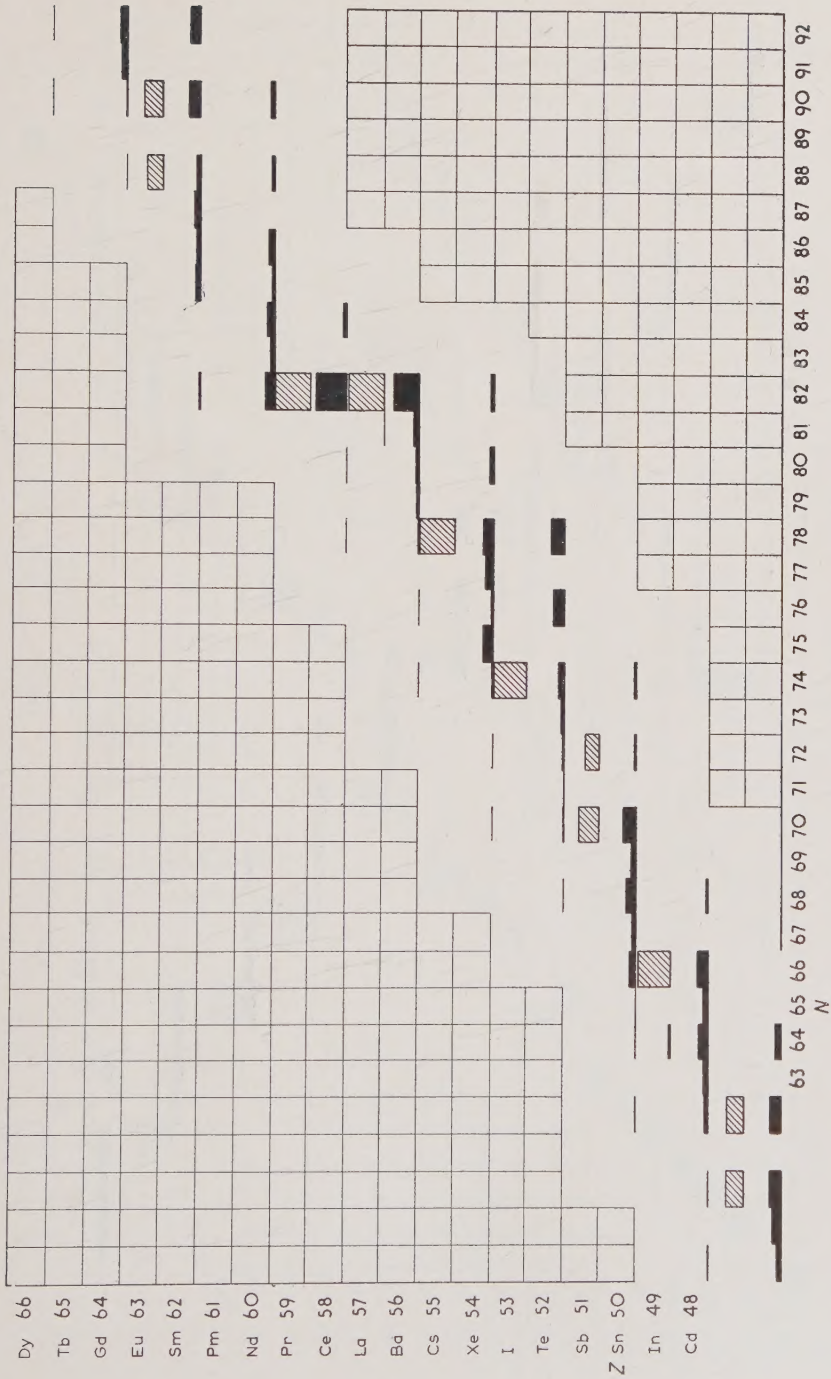
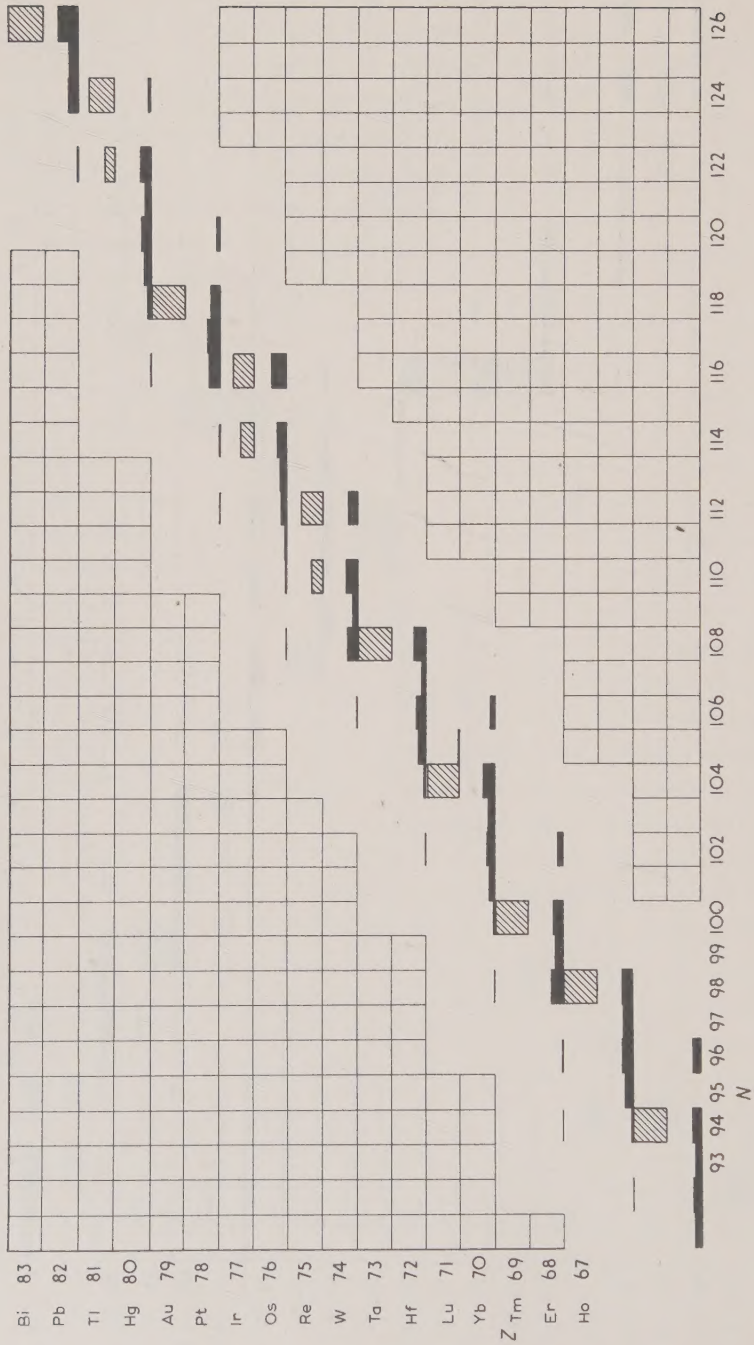

Dy 66
Tb 65
Gd 64
Eu 63
Sm 62
Pm 61
Nd 60
Pr 59
Ce 58
La 57
Ba 56
Cs 55
Xe 54
I 53
Te 52
Sb 51
Z Sn 50
In 49
Cd 48
63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92
N

Fig. 3


Bi 83
Pb 82
Tl 81
Hg 80
Au 79
Pt 78
Ir 77
Os 76
Re 75
W 74
Ta 73
Hf 72
Lu 71
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Tm 69
Er 68
Ho 67
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N

Fig. 4

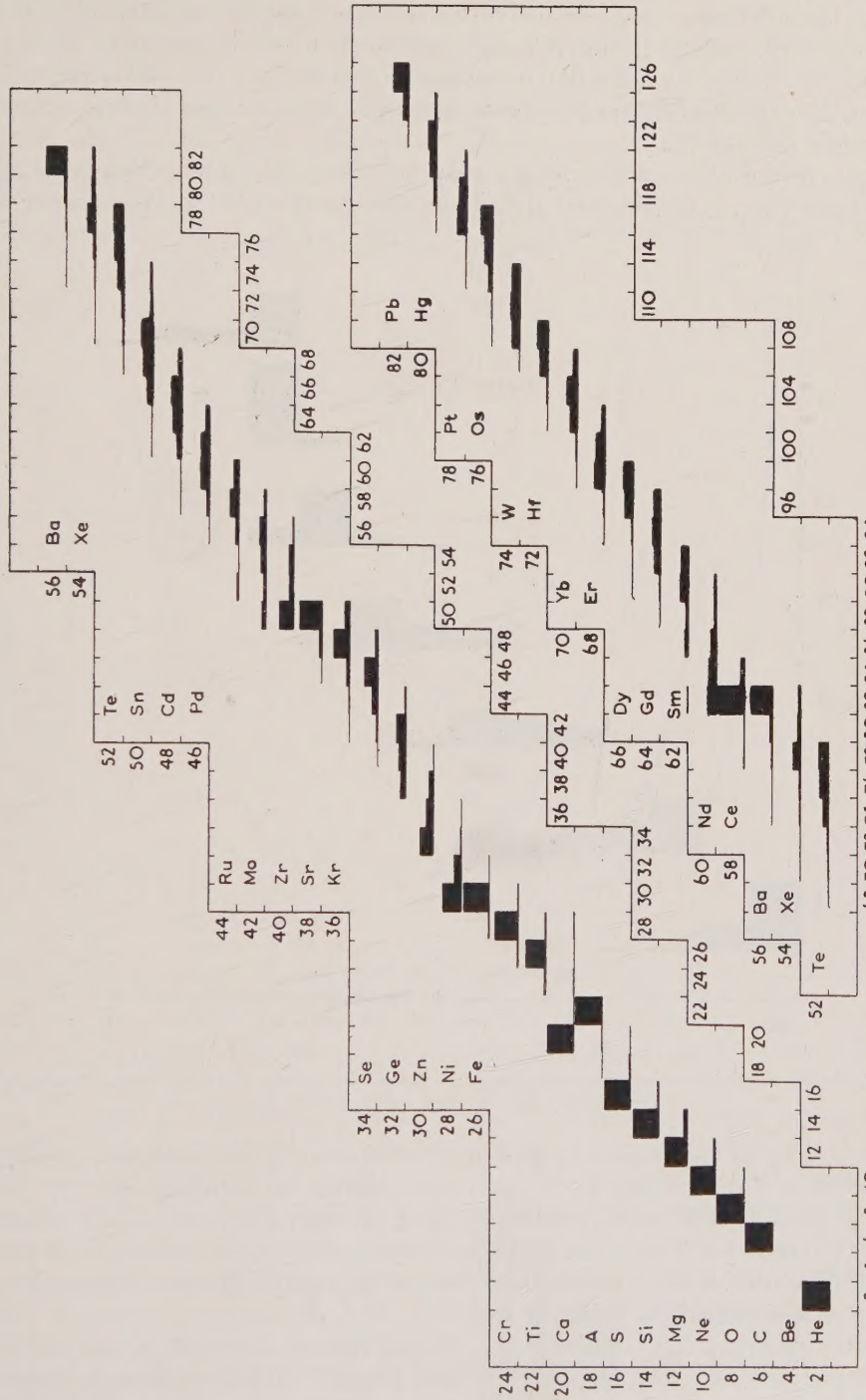

Fig. 5. As in Figs. 1–4, but for even Z, even N species only.

profound and regular of its kind; Ni, Zn, Ge, Se, Kr, and Sr are the participants. In nickel, the relative-abundance distribution slope is steeply positive (sloped down toward the high N limit), and becomes less so in zinc; in germanium, the distribution slope is slightly negative, but steepens regularly as $N = 50$ is approached. The neutron excess crossover involving principal isotopes—see below—occurs at Ga, between Zn and Ge.

Aspects of the above development may be examined more critically in Fig. 7, which relates percentage relative abundance on an expanded ordinate scale, to N,

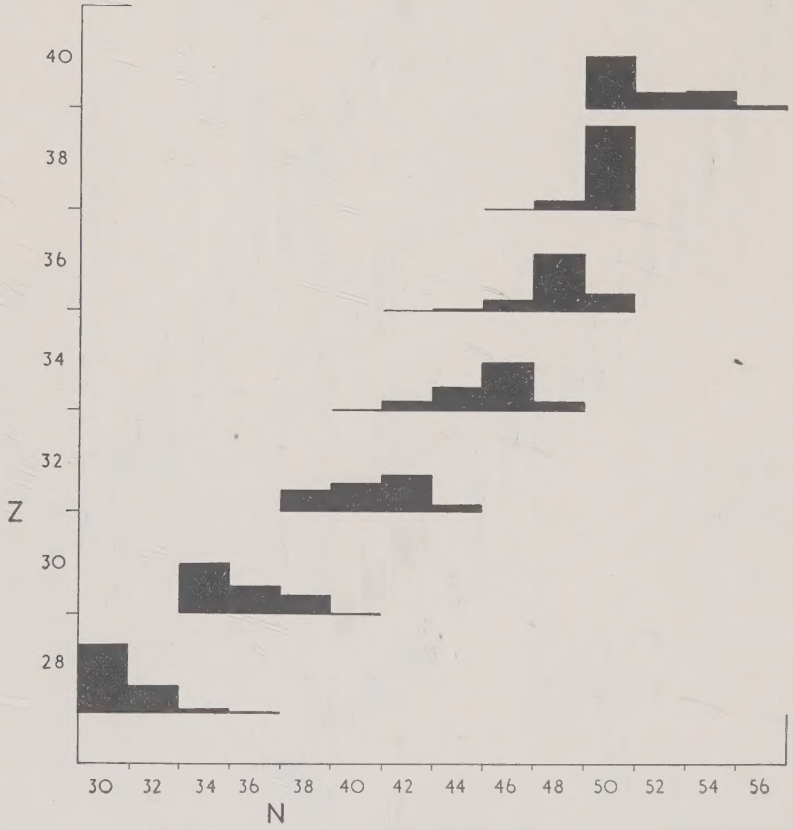

Fig. 6. N, Z relative abundance diagram for region $N = 30$ to $N = 50$ (even Z, even N isotopes only). Z scale twice that of N.

in three or four of the main isotopes of each of the six above elements. Relative abundances of the even Z, odd N species are shown for comparison.

The profound relative-abundance changes between $Z = 28$ and $N = 50$ appear to apply to the even N isotopes only; neither the relative abundance nor the N,Z route of the odd N species seems to have been seriously influenced by the cause of the even N abundance variations.

The conspicuous abundance maximum of iron in meteorites has often been emphasized; see, for example, ALPHER and HERMAN (1953). No clear correlation between this feature and the relative-abundance variations in Fig. 5 is apparent.

We may note, however, that Fe^{56}, the principal isotope of iron, is the last member of a short isodiapheric sequence of centrally disposed dominant principal isotopes (Ti^{48}, Cr^{52}, and Fe^{56}) and immediately precedes nickel, the first member of the development between $N = 30$ and $N = 50$.

At $N = 50$ we may compare relative-abundance distribution of Sr (—ve) with Zr (+ve). At $N = 82$ (a very highly favoured neutron number) similar relationships are found and also to a slight extent at $N = 98$ and $N = 116$. A great variety of relative-abundance distribution patterns are found between $N = 50$ and $N = 126$ (the maximum stable neutron number), but there is no marked tendency for these

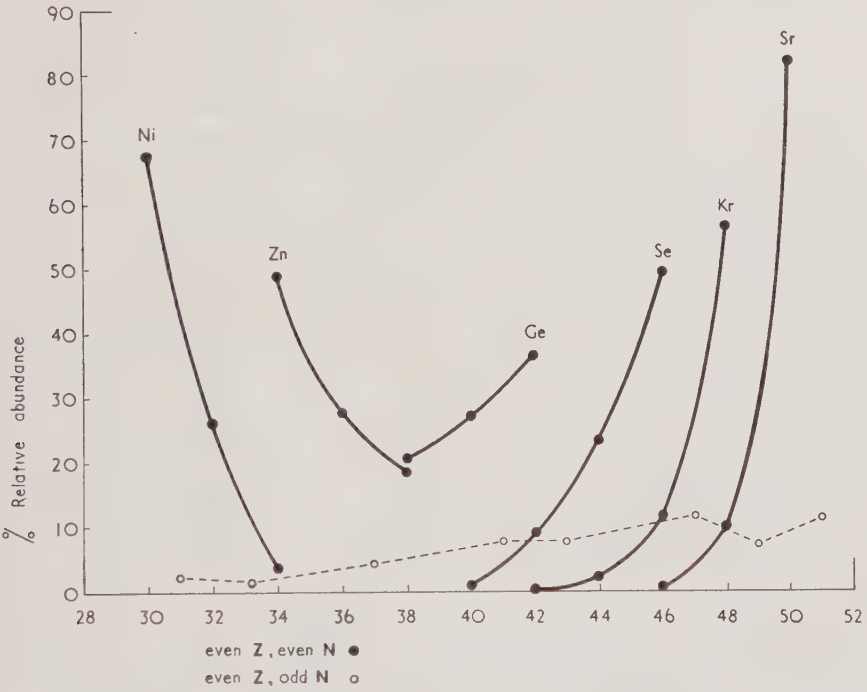

Fig. 7. The relationship between percent relative abundance and N for even Z, even N and even Z, odd N isotopes for region $N = 30$ ($Z = 28$) and $N = 50$.

patterns to participate in a development such as in the range $N = 30$ to $N = 50$. Slight tendencies of this type may be observed, however, particularly between $Z = 76$ (Os) and $Z = 82$ (Pb). The development which culminates with a relative-abundance elevation at $N = 126$ (Pb^{208}) may be examined in Fig. 8.

The isotope constitution of lead has been measured by many workers (see Rankama, 1954, for example) and the relative abundances indicated in Fig. 8 may be regarded as typical of that given in relative-abundance tables and charts. Such an isotope constitution is equivalent to that anticipated for recent lead, a mixture of original or primeval lead and radiogenic lead produced by U^{238}, U^{235}, and Th^{232}. As we go back in time, the proportions of Pb^{204}, Pb^{206}, and Pb^{208}, as well as the odd N species, Pb^{207}, change (see, for example, Fig. 9.2 of Faul, 1954). However, the general relative-abundance pattern of $Pb^{208} \gg Pb^{206} > Pb^{204}$, as

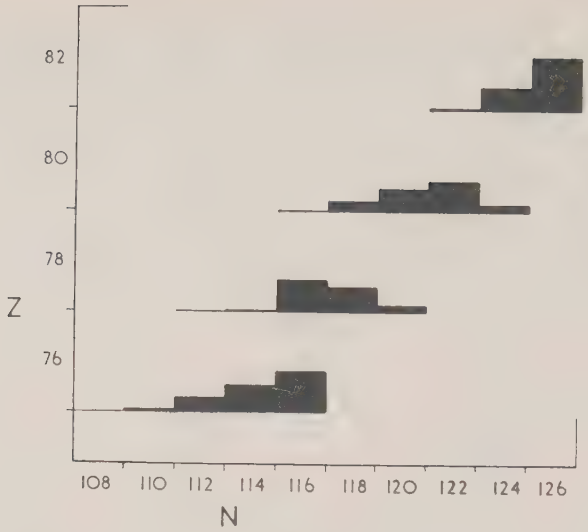

Fig. 8. As in Fig. 6, but for region $N = 108$ to $N = 126$.

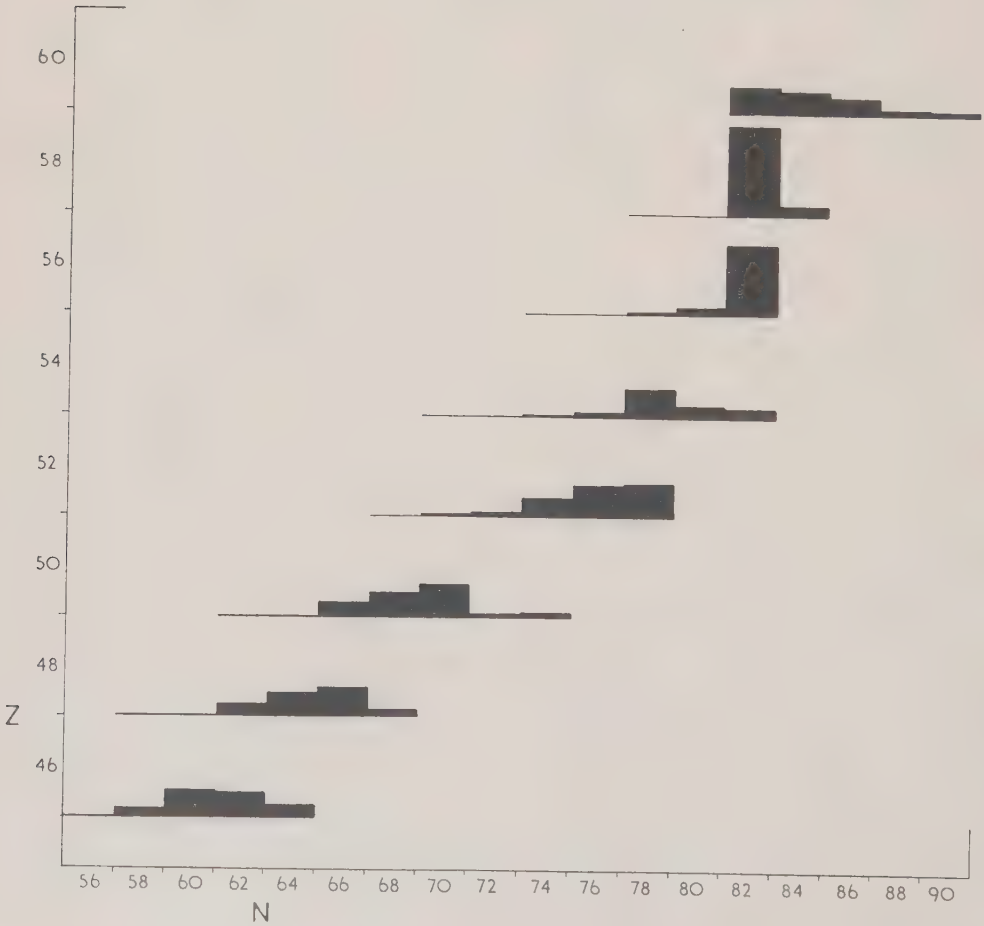

Fig. 9. As in Figs. 6 and 8 but for region $N = 56$ to $N = 90$.

indicated in Fig. 8, is not seriously modified. The most significant change concerns Pb^{208}, the principal lead isotope. Its relative abundance now is ~52%, but using the isotope constitution of Pb separated from some meteorites as a guide (see PATTERSON, 1955, which includes reference to other relevant papers), the relative abundance of Pb^{208} in primary lead appears to be elevated to about 60%.

A displacement at $Z = 52$ (tellurium) is evident in Fig. 5 and is shown more distinctly in Fig. 9. Several observations concerning this displacement may be made: first, the displacement itself. There is a displacement of the low N stability limit from $N = 66$, the expected value from the N,Z stability trend between $N = 50$ and $N = 82$, to $N = 68$. A much more profound displacement, however, is that of the relative-abundance distribution of the even Z, even N isotopes (Fig. 9). Distribution at $Z = 52$ is strongly skewed, with Te^{130} ($N = 78$) the principal isotope, forming the high N limit and displaced by $4N$ from the maximum relative-abundance trend; also the odd Z nuclide, I^{127}, has $N = 74$ and is not displaced; see principal isotope diagram (Fig. 19). In other words, the relative-abundance distribution of even Z, even N species at $Z = 52$ is banked against the high N stability limit, as may happen when a favoured neutron number is involved or approached, but in this case the development represents a displacement or discontinuity and is not part of a general trend. In some respects the tellurium displacement resembles the development at $Z = 28$, $N = 30$ (Ni^{58})—Fig. 5. There the even N relative-abundance distribution is banked against the low N stability limit; nickel, however, is the first participant of the $N = 30$ to $N = 50$ relative-abundance development, whereas the development at $Z = 52$ appears as an isolated event.

The most prominent feature which appears to be closely connected with the tellurium displacement involves the relative abundances of the odd N isotopes. Their relative abundances are quite low in tellurium, but in xenon ($Z = 54$) there are two abundant odd N relative abundance (see Fig. 10 below). Except for beryllium, this is the only example of an even Z element with total odd N relative abundance greater than total even N abundance. Also, the even N isotope Xe^{130} ($N = 76$) is much less ($\times\frac{1}{6}$) abundant than its neighbouring odd N isotopes, Xe^{129} and Xe^{131} ($N = 75$ and $= 77$), which is quite exceptional. These developments at $Z = 52$ and $Z = 54$ are clear in relative abundance charts (AHRENS, 1956c).

There seems to be some correlation between the tellurium displacement and abundance variation in meteorites. Though not very accurately known, there is little doubt that the tellurium abundance in meteorites is very low indeed. As a result, the even Z abundance curve falls sharply at $Z = 52$ and actually drops far below the odd Z abundance curve (see Fig. 9.1 of RANKAMA, 1954), a relationship which is very exceptional and is reversed immediately after tellurium.

Relative Abundances of Even Z, Odd N Isotopes

The relative abundances of even Z, odd N isotopes are related to N in Fig. 10. Odd N isotopes Sr^{87}, Te^{123}, Cd^{113}, In^{115}, and Os^{187}, which are neighbouring isobars of odd Z, even N species (see below), several measurably radioactive, are distinguished by hatching. In general, relative abundance tends to be depressed in

the light elements, due perhaps to the presence in them of dominant ($> \sim 80\%$ or so) principal even N isotopes. Once the relative abundance of the principal even N isotopes drops significantly, that of the odd N species may increase, but variations of the relative abundances of these isotopes appear to follow routes of their own, often unaffected by developments which influence the even N isotopes. This is apparent to some extent in Fig. 2 and particularly in Fig. 7. Also the effects of highly favoured neutron numbers might not make themselves felt. Cerium is a distinct exception. This element is located at the centre of the development at $N = 82$ (see Fig. 3), and the relative abundance (88.5%) of its principal isotope

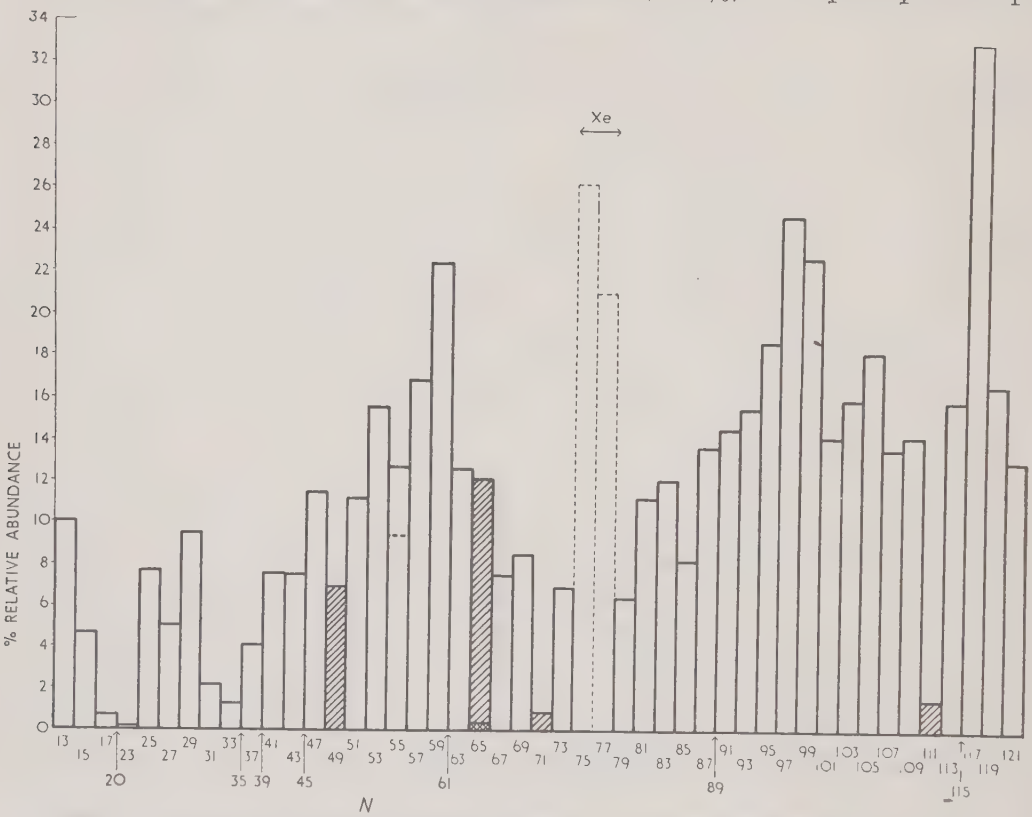

Fig. 10. Variation of relative abundance of even Z, odd N isotopes with N. Diagonal lines refer to isotopes which are neighbouring isobars of odd Z, even N species. Horizontal dashed line at $N = 55$ indicates isotonic pair. The alpha active Sm^{147} ($N = 85$) has been omitted.

(Ce^{140}; $N = 82$) is greatly elevated (Figs. 3 and 18). The effect is apparently so great that cerium does not contain any odd N isotopes.

Starting at $N = 33$, relative abundance tends to increase with N, reaching a maximum at $N = 59$ in palladium. Relative abundance drops again, but is sharply elevated at $N = 75$ and $N = 77$. As both these isotopes belong to xenon, an element with an unusual isotope-abundance distribution, they have been distinguished by dashed lines in Fig. 10. The development at xenon appears to be connected with the tellurium displacement (see above). Slight apparent abundance

depression at $N = 79$ might be due to the presence of $N = 82$ in barium, which has caused elevation of the principal isotope (Ba^{138}) in barium; Figs. 3 and, particularly, 18. The effect is not nearly so marked as in cerium.

Relative abundance increases fairly regularly from $N = 81$ to $N = 97$, after which variation is more erratic. A maximum is reached at $N = 117$; this corresponds to Pt^{195}, the only example of an odd N isotope which is a principal isotope. The trends between $N = 81$ and $N = 97$ are shown more clearly in Fig. 11. The low abundance at $N = 85$ (Nd^{145}) may be noted. Nd^{145} is isotonic with α-active Sm^{147}.

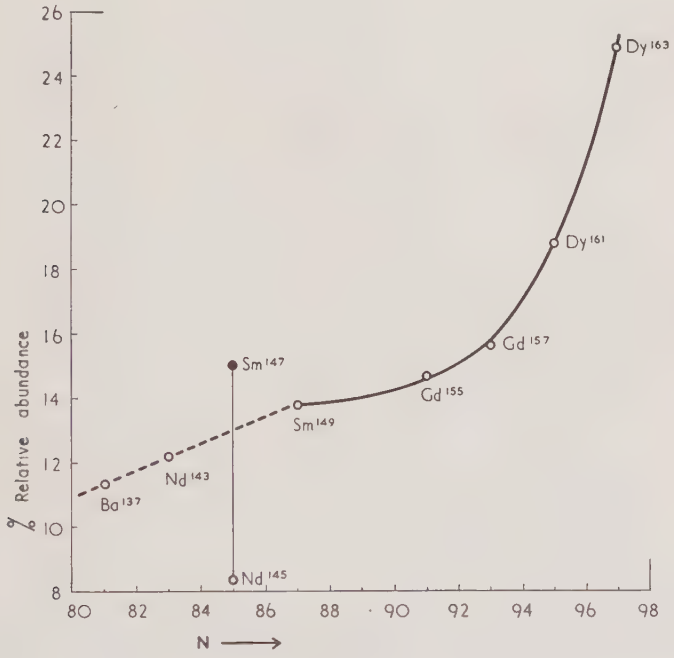

Fig. 11. Even Z, odd N isotopes; detail of development between $N = 81$ and $N = 97$.

The relative abundances of several of the odd N isotopes which are neighbouring isobars of odd Z, even N species appear to be lower than the relative abundance variations of the other odd N isotopes would indicate.

Except perhaps for the low N range, the missing neutron numbers seem to bear no relationship to the relative-abundance trends in Fig. 10.

Odd Z Elements with two Even N Isotopes

Introduction

Thirteen odd Z elements contain two even N isotopes ($\Delta N = 2$). Inspection of Figs. 1 to 4 shows them to occur over the range $Z = 17$ to $Z = 81$; the range $Z = 17$ to $Z = 37$ contains four (Cu, Ga, Br, and Rb). Eight (K, Cu, Ga, Br, Ag, Eu, Ir, and Tl) are associated with the eight missing neutron numbers, and one,

potassium, is associated with unstable $N = 21$ (K^{40}). Three (Rb, Sb, and Re) contain one isotope which is a neighbouring isobar, and one, indium, has both its isotopes as neighbouring isobars. The relevant data on these elements which will serve for our main discussion are given in Table 1; the elements have been grouped as indicated above.

Discussion

Fig. 12 relates the relative abundance of the heavier isotope in each of the thirteen elements of Table 1 to Z. A general trend of increase of relative

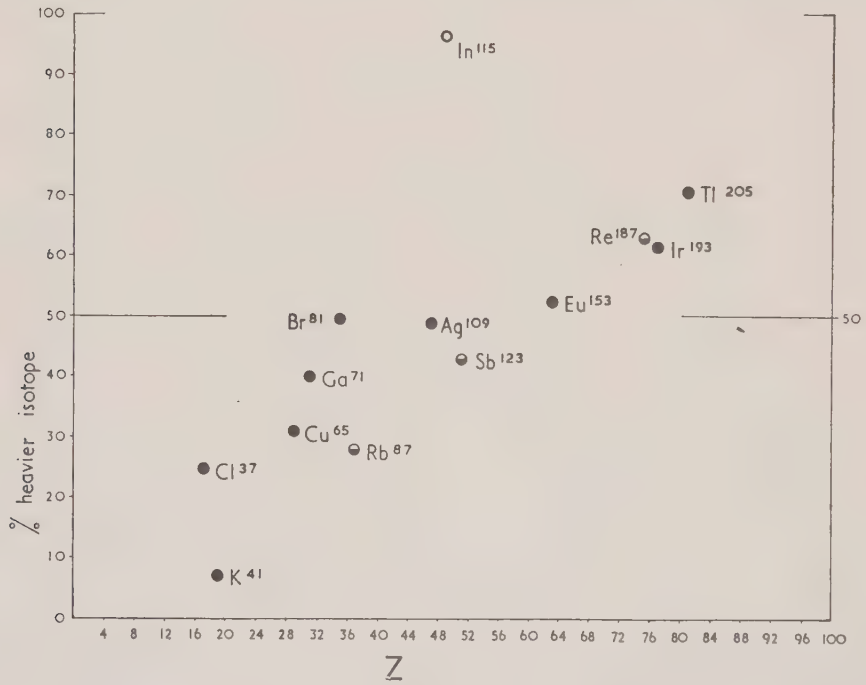

Fig. 12. Odd Z, even N isotopes. Variation of relative abundance of heavier component with Z (all elements of Table 1). The distinction of isotopes (●, ◒, ○) is according to the groups of Table 1(a), (b), and (c).

abundance with Z is clear. Within the general trend, distinct groups may be distinguished: this may be indicated more sensitively in Fig. 13, a similar diagram, in which, however, the per cent of the most abundant of each pair (Table 1(a) only) is related to N. The regularity involving Ag, Eu, Ir, and Tl appears to be quite well developed and appears to resemble an inverted growth curve with its origin somewhere in the neighbourhood of $N = 126$, the maximum stable neutron number. Primakoff (1955) has suggested that the general tendency of the relative abundance of the heavier isotope to increase with Z (or N) might be due to the neutron-excess increase with increase of Z (or N). Fig. 14 relates the relative abundance of the light isotopes (Ag^{105}, Eu^{151}, Ir^{191}, and Tl^{203}) to the difference between the neutron excess (43) in Bi^{209}, the heaviest stable odd Z

Table 1. Odd Z elements with two isotopes ($\triangle N = 2$)

(a) Those associated with the eight missing neutron numbers and $N = 21$

Element	Z	N	Per cent relative abundance
Cl	17	18	75·4
		20	24·6
K	19	20	93·1
		22	6·9
Cu	29	34	69·1
		36	30·5
Ca	31	38	60·2
		40	39·8
Br	35	44	50·5
		46	49·5
Ag	47	60	51·35
		62	48·85
Eu	63	88	47·8
		90	52·2
Ir	77	114	38·5
		116	61·5
Tl	81	203	29·5
		205	70·5

(b) Elements with one isotope as a neighbouring isobar

Element	Z	N	Per cent relative abundance
Rb	37	48	72·15
		50	27·85
(Neighbouring isobar, Sr^{87}, has $N = 49$)			
Sb	51	70	57·25
		72	42·75
(Neighbouring isobar, Te^{123}, has $N = 71$)			
Re	75	110	37·07
		112	62·93
(Neighbouring isobar, Os^{187}, has $N = 111$)			

(c) Both components are neighbouring isobars

Element	Z	N	Per cent relative abundance
In	49	64	4·23
		66	95·77

(The neighbouring isobars, Cd^{113} and Sn^{115}, each have $N = 65$)

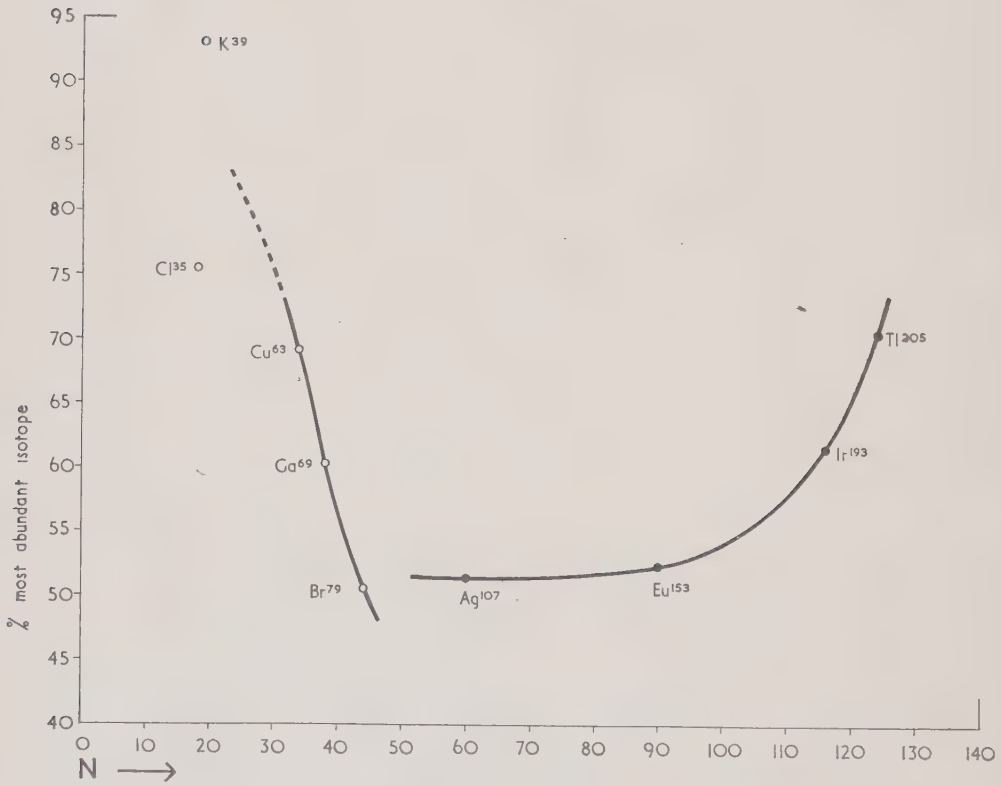

Fig. 13. Variation of relative abundance of most abundant isotope with N (9 elements of Table 1(a)).

element ($N = 126$), and that of the isotope in question. The relationship is well developed and becomes linear, or very nearly so, when log $(43 - N + Z)$ is related to relative abundance (Fig. 15). The equation for the line as drawn is:

$$\text{Per cent relative abundance} = 18{\cdot}5 \log \Delta + 24 \qquad (1)$$

where $\Delta = 43 - (N - Z)$. When $\Delta = 1$, the relative abundance is 24%. Table 2 compares relative abundances calculated from Equation (1) with the original measurements used for preparing Figs. 14 and 15.

Table 2. A comparison of relative abundance values

Isotope	Neutron excess difference	Per cent		Difference
		Equation 1	Original measurements	
Tl^{203}	2	29·57	29·46	0·09
Ir^{191}	6	38·4	38·5	0·1
Eu^{161}	18	47·2	47·77	0·57
Ag^{107}	30	51·32	51·35	0·03

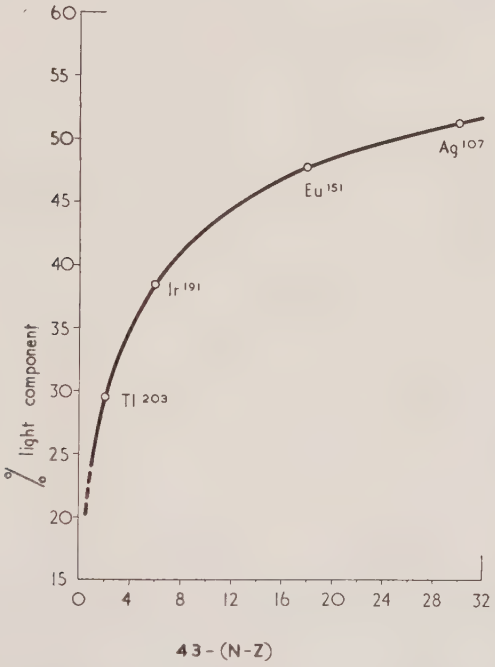

Fig. 14. Odd Z, even N isotopes. Variation of relative abundance of light component of Tl, Ir, Eu, and Ag with neutron excess difference (see text).

Relative abundances of Tl, Ir, and Ag isotopes are from White and Cameron (1948) and Eu isotopes from Hess (1948). The difference in each example is small; the maximum (Eu^{151}) is $\sim 1\%$. Using as a guide the conclusions of White and Cameron (1948) who have considered the problem of mass spectrometric error in detail, these individual deviations should probably be within the limits of experimental error. In this general respect we should note that relative-abundance measurements on Tl^{203}, Ir^{191}, and Ag^{107} have been made in one laboratory over a limited period (White and Cameron, 1948), whereas that on Eu^{151}, the measurement with greatest deviation, has been made in another (Hess, 1948).

Fig. 15 also shows the relationship between log $(43 - N + Z)$ and percentage relative abundance for the heavier isotope in each pair. The neutron excess of each of these isotopes is two less than the lighter one, and in $Tl^{205} = 43$. This is the same as that Bi^{209} (and Pb^{208}), and hence $\Delta = 0$. In the semilogarithmic plot (Fig. 15), Tl^{205} has been given an abscissal value of one.

The regularity involving isotopes of Cl, K,Cu, Ga, and Br is not so well developed as that involving isotopes of Tl, Ir, Eu, and Ag, and this may be due to the effect of $N = 20$. Fig. 16 relates per cent relative abundance of the heavy isotope of Cl,

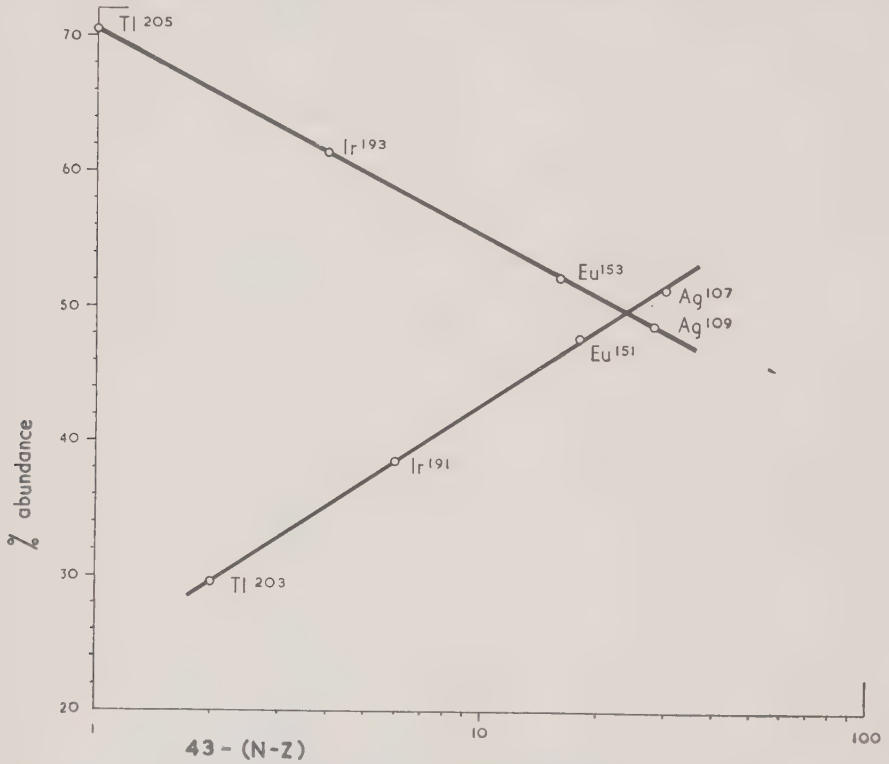

Fig. 15. As in Fig. 14, but on semi-logarithmic co-ordinates.

K, Cu, Ga, and Br to $N - Z$. It is possible that the relationship is linear, as drawn, and the line through Ga and Cu passes through the origin and very close to Br—probably to within the limits of experimental error. Clear evidence of the effect of a highly favoured neutron number on the relative abundances of even Z, even N isotopes is indicated below (Fig. 18), and it seems quite possible that $N = 20$ might elevate the relative abundances also of odd Z, even N species. Cl^{37} has $N = 20$, and accordingly its relative abundance may have been elevated, whereas in the pair K^{39}–K^{41}, the lighter component has $N = 20$, and if its abundance has been elevated, that of K^{41} would be depressed. This might account for the displacement of Cl^{37} and K^{41} in Fig. 16.

The relationship between the neutron excess and the relative abundance of the heavier isotope of Rb, In, Sb, and Re is shown in Fig. 17: Rb^{87}, Sb^{123}, and Re^{187}

appear to participate in a regularity, whereas In^{115} is distinctly displaced. It will be recalled that indium is the only odd Z element with both its isotopes as neighbouring isobars. The Rb^{87}—Sb^{123}—Re^{187} "isobaric" regularity appears to be quite distinct from the two "missing neutron number" regularities which are shown in Fig. 17 for comparison. Rb^{87} and Re^{187} are, however, measurably radioactive with probable half-lives 4·3 to 6·0 $\times$ 10^{10} years (see AHRENS, 1956, for literature survey) and 5·0 $\times$ 10^{10} years (HERR, HINTENBERGER, and VOSHAGE,

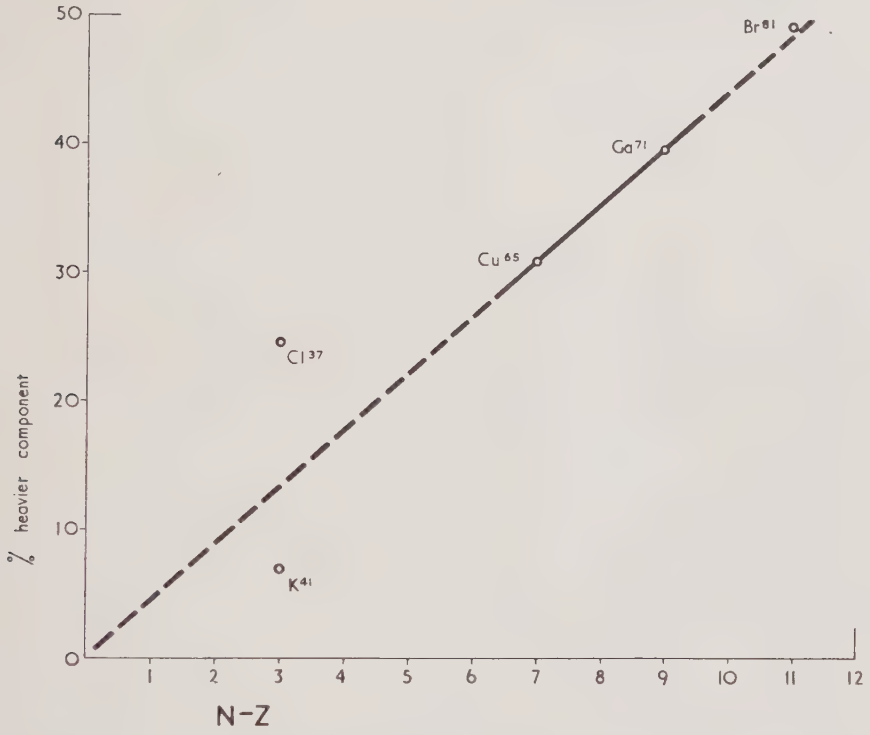

Fig. 16. Odd Z, even N isotopes. Variation of relative abundance of light component of Cl, K, Cu, Ga, and Br with neutron excess.

1954) respectively. Although these half-lives are long when compared with the probable age magnitude of formation of the elements, which is estimated roughly at one-tenth of the half-life magnitude (see AHRENS, 1956b, for survey of some relevant age data), allowance for the decay of Rb^{87} and Re^{187} modifies the nature of the Rb^{87}—Sb^{134}—Re^{187} relationship quite significantly. The curvature tends to straighten, and linearity obtains at about $\sim$5000 $\times$ 10^6 years (Fig. 17). It is difficult to assess the possible significance of this observation. Only three elements are involved, and there is still some uncertainty about the decay constants of Rb^{87} and Re^{187}; also, Rb^{87} has $N = 50$, a highly favoured neutron number, and its abundance may therefore be elevated. This is, of course, a definite possibility, but on the other hand we should not overlook the fact that linearity, or a very close approach to it, does hold if allowance is made for decay over a period 5000 $\times$

10^6 years or so; perhaps radioactive species such as Rb^{87} are immune from the anticipated effect of highly significant $N = 50$.

Some observations may be made concerning neighbouring isobars, when one isobaric component is an isotope of an odd Z element containing two even N isotopes. First, in each of the three examples of measurable activity, it is the odd Z, even N species which is β-active (Rb^{87}, In^{115}, and Re^{187}), decaying to the stable even Z, odd N species. *Purely* from this consideration only, Sb^{123} would be

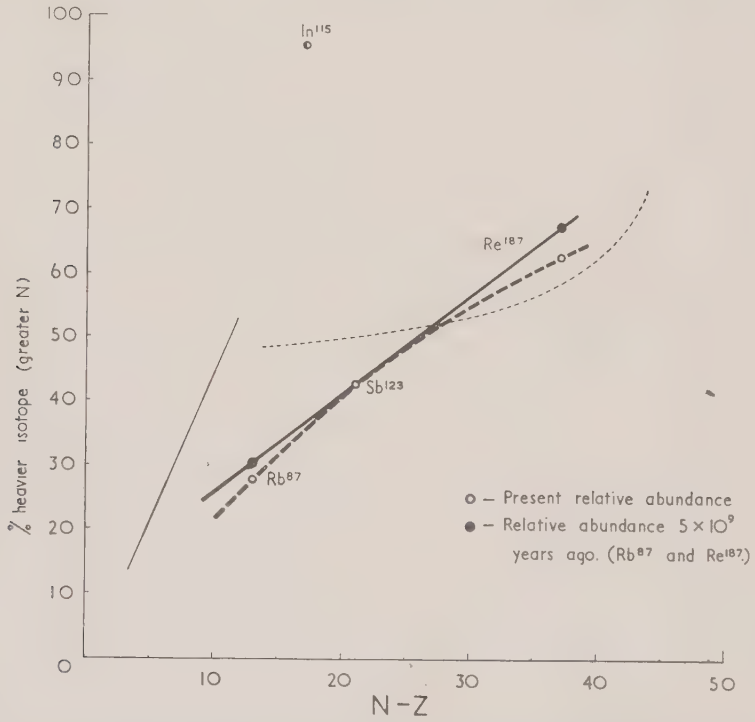

Fig. 17. Odd Z, even N isotopes. As in Fig. 14, but for elements which have either one (Rb, Sb, and Re) or both (In) isotopes as neighbouring isobars.

predicted as the unstable component in the pair Sb^{123}—Te^{123}. Second, it is the heavier isotope in each of these odd Z elements which is unstable; and third, the relative abundance of the always-stable (even Z, odd N) component of the neighbouring isobaric pair sometimes tends to be low—see under even Z, odd N isotopes.

The presence of two isotopes in thirteen odd elements and the existence of well developed relative-abundance relationships within groups, raises the question as to whether such species are seriously distinct from the other odd elements, and, if so, whether such a difference is likely to influence cosmic abundance. We should wish to critically examine cosmic-abundance relationships in the groups Cl, K, Cu, Ga, and Br; Ag, Eu, Ir, and Tl; and Rb, Sb, and Re, and compare their abundances with the general trend of the odd Z abundance curve. The available data are as yet not accurate enough for a critical comparison of this type.

Principal Isotopes

Introduction

A principal isotope will refer to the most abundant isotope of an element; such an isotope may therefore be either really dominant—up to 100% for elements with one isotope—or, at the other extreme, one which is only very slightly more abundant than the next most abundant isotope. In a paper on nuclide systematics, Breusch (1946) has discussed some relationships involving principal isotopes, and Ahrens (1956a), in a discussion on cosmic abundances, has referred briefly to the nature of the $N - Z$ vs. Z relationship for the principal isotopes in several elements. We shall briefly examine, first, variation of relative abundance of principal isotopes of even and odd elements, with respect to Z, and then consider their N,Z relationship.

Variation of Relative Abundance with Z

Fig. 18 relates the relative abundances of the principal even Z isotopes to $Z = 82$. Up to Z and $N = 20$, the principal even N isotope is dominant, with the exception of $Z = 4$ (Be). After Z and $N = 8$, relative abundance decreases to a minimum at Z and $N = 12$, and rises to a maximum at Z and $N = 20$. There is a sharp drop at $Z = 22$, $N = 26$; relative abundance then increases, and, following $Z = 26$, $N = 30$ (Fe^{56}), drops steadily to minimum at $Z = 32$, $N = 42$. The increase to a peak which follows is evidently due in part to the presence of $N = 50$. After $Z = 40$, $N = 50$ (Zr^{90}), relative abundance drops to a minimum at $Z = 42$, $N = 56$, and thereafter remains more or less uniform at ~30% up to $Z = 82$, save for an abrupt and very conspicuous interruption at $Z = 56$ and $Z = 58$ (Ba and Ce), due clearly to the presence of highly favoured $N = 82$. At $Z = 82$ ($N = 126$), relative abundance increases again, and this is evidently due to the effect of favoured $N = 126$. A slight but distinct abundance elevation at $Z = 76$ ($N = 116$) is also evident.

The effect of highly favoured $N = 20$, 50 and particularly 82 on relative abundance (Fig. 18) may be compared with that on meteorite abundance. The slightly elevated abundances of Ca, Zr, and Ba (see Fig. 9.1 of Rankama, 1854) may be due to the presence of $N = 20$, 50, and 82 respectively in the principal isotopes of these elements. The effects of $N = 50$ and $N = 82$ become very distinctly apparent, however, if meteorite abundance of even Z, even N isotopes is related to N (not shown); abundance elevation at $N = 50$ is due mainly to isotonic $Sr^{88} + Zr^{90}$ and at $N = 82$ to isotonic $Ba^{138} + Ce^{140} + Nd^{142}$.

Odd Z elements either contain only one isotope, or, if they contain two, relative abundance varies as discussed above under odd Z, even N isotopes. Which of the two isotopes is the principal one is determined by the nature of the regularities shown in Figs. 12—17.

The N,Z Relationship for Principal Isotopes.

With the exception of the five nuclides A^{36}, Br^{81}, Pd^{108}, Ag^{109}, and Pt^{194}, the N,Z diagram shown as Fig. 19 refers only to principal isotopes. A^{40} is the principal isotope of argon as measured now, but, for reasons already noted, A^{36} is plotted

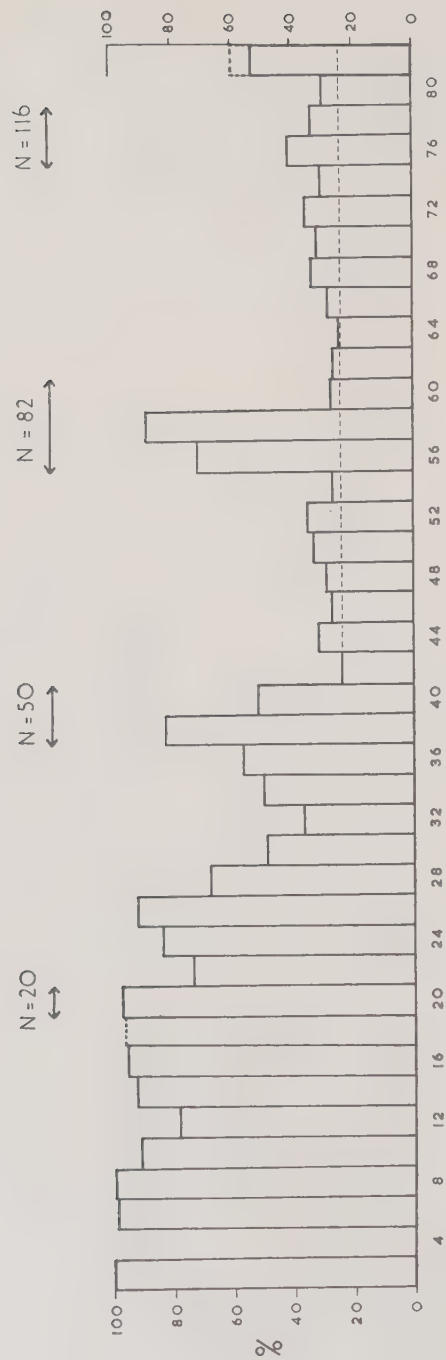

Fig. 18. Variation of relative abundances of principal even Z isotopes with Z. Pb^{203} dashed line indicates probable value of Pb^{208} some $4–5 \times 10^9$ years ago. See text.

in Fig. 19. Se^{80}, the principal isotope of selenium, is isotonic ($N = 46$) with Br^{81} (49·48%) rather than Br^{79} (50·52%), but as the relative-abundance difference is very small, Br^{81} has been plotted in Fig. 19, but in parentheses. Two other parenthesized points appear in Fig. 19, namely the isotonic pair Pd^{180} and Ag^{109} with $N = 62$. Neither is a principal isotope, because $Ag^{109} = 48{\cdot}65\%$, as compared with $Ag^{107} = 51{\cdot}35\%$, and Pd^{108} (26·8%) is slightly less than Pd^{106} (27·2%). As the differences are very small, the behaviour of these nuclides does not seem to be seriously exceptional, and they have been plotted in Fig. 19 because of their precise fit on the sequences following $N = 50$. In platinum, the even N isotope

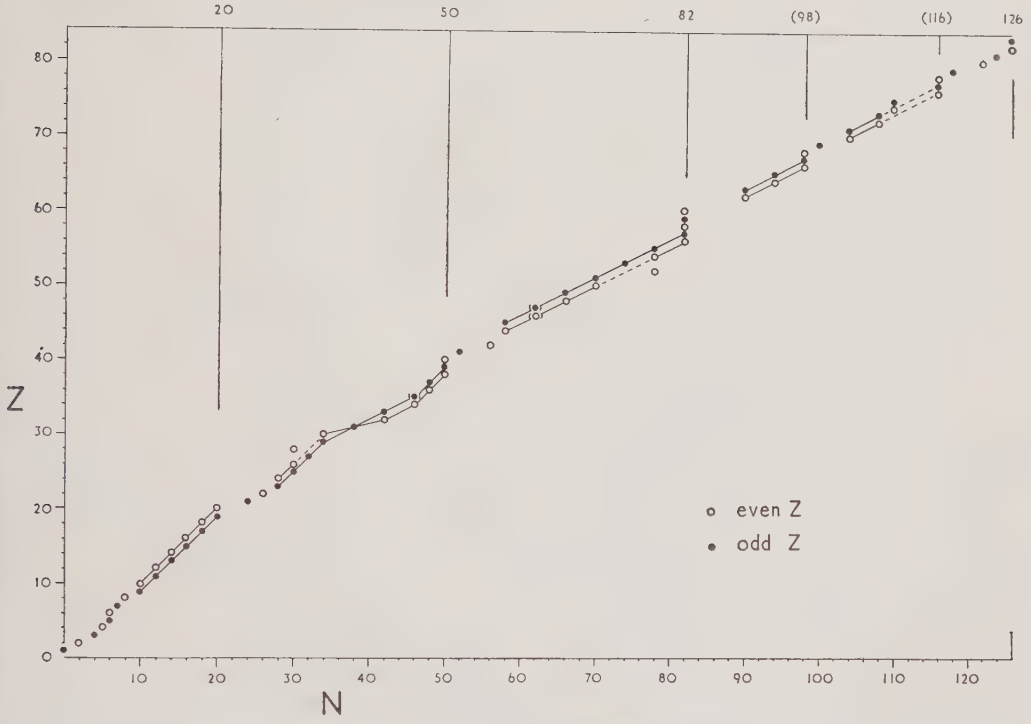

Fig. 19. N,Z diagram for principal isotopes.

Pt^{194} (32·8%) has been plotted in place of the exceptionally abundant odd N isotope, Pt^{195} (33·8%).

Principal discontinuities in Fig. 19 are clear at the well-established favoured neutron numbers $N = 20$, 50, and 82, and serve to divide the diagram broadly into three distinct regions. One characteristic common to all regions is the tendency (Breusch, 1946) of the principal isotopes of neighbouring elements ($\Delta Z = 1$) to occur as pairs of isotones. Above $Z = 8$ this rule holds fairly generally and, apart from $Z = 28$ (Ni) and $Z = 52$ (Te), is only seriously disturbed at and following $N = 20$, 50, and 82 and, to a small extent, at $N = 98$ and 116. As a consequence, odd Z and even Z sequences are parallel. We may now consider each region in turn.

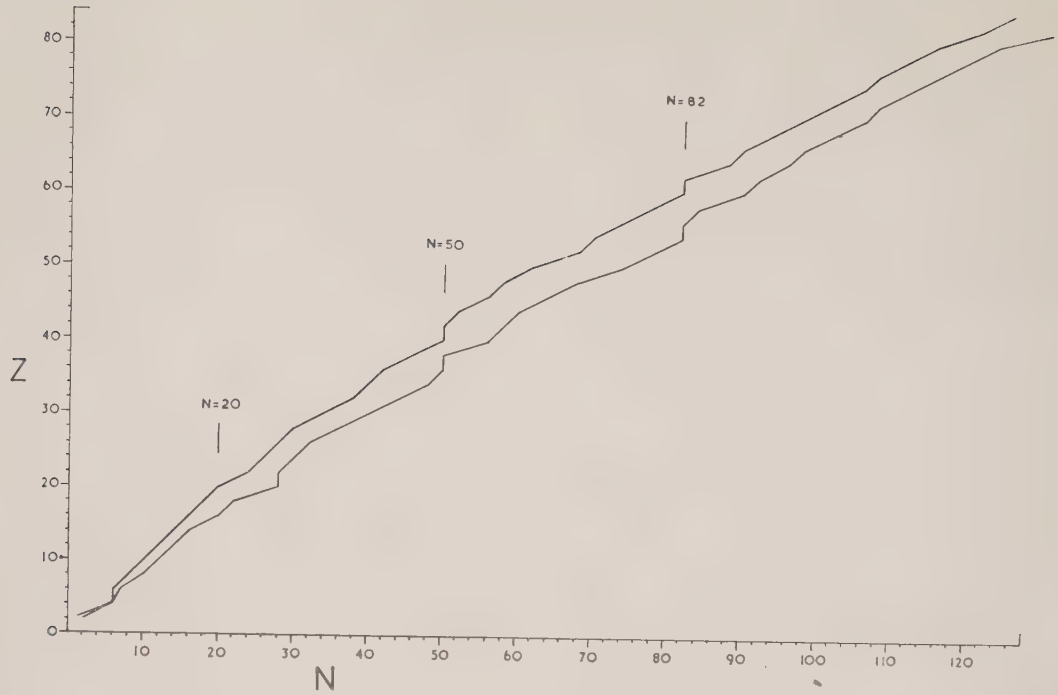

Fig. 20. N, Z stability limit diagram.

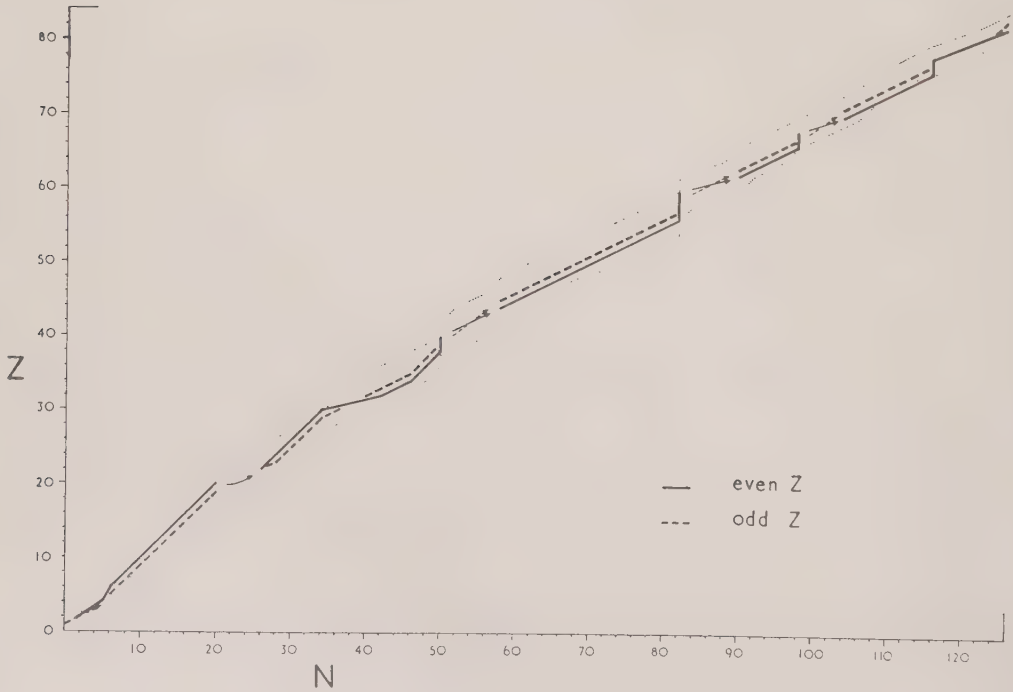

Fig. 21. Disposition of principal isotope sequences within N,Z stability limits.

In the region $Z = 1$ to $Z = 20$, principal isotopes tend to occur singly over the low Z range, but parallel isodiapheric sequences start at $N = 10$ ($Z = 9$ and 10) and terminate at $N = 20$ ($Z = 19$ and 20). The heavier member of each isotonic pair in these sequences is even Z and therefore its neutron excess is lower, by one, than the odd Z component. For the sequences in question, $N - Z = 0$ (even Z), and 1 (odd Z).

Following $N = 20$ ($Z = 19$ and 20), two principal isotopes, Sc^{45} and Ti^{48}, occur singly. Two short sequences of isodiapheres follow with Ni^{58} as an exception. Then follows an interesting development. $N - Z$ increases by two in each of several succeeding odd Z elements, but increases by six when going from Zn^{64} to Ge^{74}. The even Z curve thus crosses the odd Z curve (at Ga) and then drops below it. This relationship persists up to $Z = 82$, but is disturbed at and following $N = 50$, 82, 98, and 116. As a result of the crossover at Ga, the lighter component of each pair of isotonic principal isotopes is even Z, and therefore has the greater neutron excess. Two short isodiapheric sequences follow Ga and end at $N = 50$. The range $N > 20 < 50$ could perhaps be regarded as transitional because of the Ga crossover and because both $2p + 2n$ and $2p + 4n$ sequences are found (Fig. 19) in roughly equal proportion. It is in this region also that the variation of the relative abundances of even Z, even N isotopes is unusually regular—see under even Z, even N isotopes.

A distinctive feature about the region $N > 50$ is the presence of a succession of displaced $2p + 4n$ sequences. Three principal isotopes (Sr^{88}, Y^{89}, and Zr^{90}) have $N = 50$; thereafter two principal isotopes occur singly, followed by two parallel sequences which end at $N = 82$. Five principal isotopes (Ba^{138}, La^{139}, Ce^{140}, Pr^{141}, and Nd^{142}), a maximum for any value of N, occur at $N = 82$. There follows again a barren region, as after $N = 20$ and $N = 50$, but this time totally barren, as no principal isotopes occur singly. Sequences start at $N = 90$ and continue to $N = 98$, where three principal isotopes are found. A similar minor discontinuity takes place at $N = 116$, preceded, however, by a displacement at $N = 110$. Following $N = 116$, principal isotopes occur singly up to $N = 126$, which is doubly occupied (Pb^{208}, Bi^{209}).

Some of the developments of Fig. 19 are correlateable with abundance variations in the chondrite meteorites. The abundances of singly-occurring Sc^{45} and Ti^{48}, which follow $N = 20$, are conspicuously low in chondrites. Singly-occurring Nb and Mo follow $N = 50$, but their abundances do not appear to deviate seriously from the general-abundance trend; that of Nb is low, but not conspicuously so. The "missing" short-lived element Tc ($Z = 43$) follows $N = 50$ and another "missing" short-lived element, Pm ($Z = 61$), follows $N = 82$.

The Relationship of the Principal Isotope Sequences to the N,Z Stability Limits

Fig. 20 is an N,Z stability limit diagram, and Fig. 21 shows the disposition of the principal isotope sequences within these limits. From N and $Z = 10$ to N and $Z = 20$, the principal isotope sequences are disposed toward the upper limit, with the even Z sequence in fact forming the upper limit. At $N = 50$ and $N = 82$, the even Z principal isotope again reaches the upper stability limit curve. Between $N = 108$ and $N = 116$, the principal isotope sequences are disposed

toward the lower stability limit curve, with the even Z sequence forming the limit. It is clear that the route followed by the principal isotope sequences is quite distinct from that followed by the mass-energy valley or line of β stability (see for example, Kohman, 1948; and Fig. 3.1 of Evans. 1956), which is more or less centrally disposed with respect to the stability limit curves over the whole range of Z and N.

Note on Relative Abundance Variation and Significant Neutron Numbers

A summary of the types of evidence used to indicate the existence of significant neutron numbers may be found in Chap. 2 of Mayer and Jensen (1955). The evidence from nuclide systematics includes the presence of discontinuities at $N = 50$ and $N = 82$, for example, in an N,Z stability limit diagram such as Fig. 20. The effects of well-established significant neutron numbers are, however, much more marked in the N,Z principal isotope diagram (Fig. 19) and in the N,Z relative-abundance diagrams (Figs, 1 to 5, and Fig. 18) and accordingly these will be examined further for developments which might have significance in this respect.

The effects of $N = 98$ and $N = 116$ in Fig. 19 are similar, but not nearly so marked as those of $N = 50$ and $N = 82$, and could be regarded as somewhat favoured. Relative-abundance distribution of even Z, even N isotopes (Fig. 5) gives some support to the significance of these numbers. There is also slight but distinct relative-abundance elevation at $Z = 76$ and $N = 116$ (Fig. 18).

$N = 30$ could perhaps also be regarded as a significant number. Like $N = 50$, 98, and 116, it is trebly occupied by principal isotopes. The even N species, Fe^{56} ($N = 30$), is the last member of the Ti–Cr–Fe triad, whereas Ni^{58} ($N = 30$, $Z = 28$) is the first member of the profound development between $N = 30$ and $N = 50$. It is evident, however, that if $N = 30$ is a significant neutron number, it should be regarded as distinct from $N = 20$, 50, 82, (98, 116), and 126, because the developments associated with it appear to be quite different from those associated with the other significant neutron numbers. This applies also to possibly significant $N = 78$; see discussion above concerning tellurium displacement.

It is possible that in nickel, $Z = 28$ has particular significance rather than $N = 30$. If so, it is interesting to observe that the developments between nickel and $N = 50$ would start with a significant proton number (28) and end with a significant neutron number (50).

Neither the numbers 98 and 116, nor 30 and 78, are included in a list (Mayer and Jensen, 1955, for example) of numbers supposed to indicate total numbers of identical nucleons in subshells of current most popular models of the nucleus (see, for example, Mayer and Jensen, 1955). On the other hand, several such supposed subshell numbers do not appear to be significant in Figs. 1 to 5, and Figs. 18 and 19).

Although $N = 82$ may be the most significant of all neutron numbers, in so far that the local relative-abundance effects at $N = 82$ are much greater than at $N = 50$, the relative-abundance developments which precede it are hardly comparable with those which precede $N = 50$, which are profound and well developed and extend as far back as $Z = 28$ ($N = 30$). There is little which precedes $N = 82$

to indicate that a highly favoured neutron number is being approached. The tellurium displacement (see above), though distinct, is an abrupt development and not part of a trend leading up to $N = 82$.

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The use of monazites for age determination

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(*Received* 27 *March* 1956)

Abstract—The results of four new isotopically controlled age determinations on monazites are presented. Two of the samples exhibit gross discrepancies in their individual isotopic ages. Some acid-washing experiments have been made on the powdered samples which give correlations with the age patterns. Specifically, high U^{238}/Pb^{206} ages are accompanied by excessive solubilities of uranium relative to thorium and Pb^{206} relative to Pb^{208} in the acid washes. The problem of the cause of the discordant ages is discussed with the aid of these data.

Introduction

The papers of Nier, Holmes, and co-workers record nine age determinations on monazites, which include isotopic analyses of their leads. With one exception, these analyses give discrepancies among the uranium-lead, thorium-lead, and lead ages which greatly exceed experimental errors. The present work lists the results of four new isotopically controlled age determinations on monazites and describes some acid-washing experiments which aid in the interpretation of the age discrepancies. An account of the stratigraphic implications of the age determinations has been given by Nicolaysen (1954), and this aspect will be treated in a separate publication.

New Monazite Age Determinations

Description of Samples

The Steenkampskraal specimen was collected by Nicolaysen in the Van Rhynsdorp district of the Cape Province, South Africa. It occurred six feet below the surface exposures, in the sheet-like monazite-bearing ore body which parallels the gneissic foliation. It consists of a massive granular aggregate of monazite and titanomagnetite. The monazite crystals average 0·2 to 0·3 mm in diameter; in thin section they have a clouded appearance, owing to the presence of haematite in films and cracks.

The Goodhouse monazite was supplied by Dr. D. J. Simpson. It occurred in a pegmatite on the farm Amam, fifteen miles south-east of Goodhouse in the western Orange River region of the Cape Province (*Union Geological Survey Atomic Energy Division Museum Catalogue* No. D/67/51). The analysed material consisted of a well-formed crystal approximately 2 cm in length, which was free from cloudiness or inclusions. The general geology of these pegmatites has been described by Gevers, Partridge, and Joubert (1937).

The Houtenbek sample was provided by Professor L. C. de Villiers, of the Geological Survey Museum, Pretoria. The label indicated that the specimen was from the locality described by Lombard (1931), on the farm Houtenbek 392 in the Moos River district of the Bushveld Igneous Complex. The crystals were

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2 to 3 cm in length, and showed signs of alteration, with thin films of a light brown mineral present on many cleavage planes. In thin section the monazite is fresh, except for the presence of this (unidentified) mineral, which also appears in cracks extending outwards from the cleavage planes. Haematite-bearing veins also extend from the monazite into the surrounding matrix of quartz.

The Brown Derby monazite specimens were collected from Pit No. 11 at the Brown Derby Mine (map of STAATZ and TRITES, 1955) near Gunnison, Colorado, by a field party from the Carnegie Institution of Washington. The mineral occurred as crystals 1 to 2 cm long in a matrix of albite-quartz, which contained columbite-tantalite in addition to monazite. On microscopic examination, the monazite had a fresh appearance, slightly superior to that of the Goodhouse monazite. STAATZ and TRITES (1955) have given a detailed description of the Brown Derby pegmatites.

No marked differences were noted in the X-ray diffraction spectra of the four monazites.

Analytical Techniques

Ground samples of approximately 100 mg were fused in borax for 15 min, using a Meker burner equipped with an air blast. The borax bead was then dissolved in 3 M hydrochloric acid and the resulting solution was diluted to 100 ml in a volumetric flask. Aliquots of this solution were taken for the uranium, thorium, and lead determinations. Uranium and lead were determined by isotope dilution procedures and thorium by a colorimetric method. Outlines of the procedures follow.

Uranium. An aliquot of solution containing 15 to 30 μg of uranium was mixed with 8·1 μg of uranium with a U^{235} content exceeding 99·9%. The uranium was recovered by a series of hexone extractions from saturated nitrate solutions, and the uranium content of the sample was determined from the U^{235} to U^{238} ratio of the uranium mixture as given by a mass spectrometer. A more detailed description of these procedures has been published (TILTON *et al.*, 1955).

Thorium. A colorimetric procedure was used which closely followed that already described by TILTON, ALDRICH, and INGHRAM (1954). In brief, the sample was fused in borax and the rare-earth fluorides were precipitated, carrying thorium. The combined fluorides were dissolved in a saturated solution of aluminium nitrate enneahydrate containing 15% nitric acid by volume. Thorium was extracted into hexone, the hexone backwashed three times with the aluminium nitrate-nitric acid reagent, and the thorium finally extracted into water. The amount of thorium was determined colorimetrically by the "Thorin" method. The 24-day Th^{234}-Pa^{234} beta activity was carried through the processing to determine the yields, which varied from 65 to 75%.

Lead. Lead was isolated from the samples by extracting it into dithizone from a solution at a pH of 8·5, using citrate and cyanide to inhibit the extraction of interfering elements. The procedures were taken from those of PATTERSON (TILTON *et al.*, 1955). Three samples were processed: (1) a known weight of sample mixed with a known weight (17 μg) of a tracer lead containing 86% Pb^{206}, (2) a sample without any added tracer, (3) a blank which was measured by processing the Pb^{206} tracer through all the steps of the procedure with the same amounts of reagents. From these determinations it was possible to obtain the isotopic composition and concentration of the lead in the sample. Blanks were 0·2 to 0·3 μg, which may be compared with the 30 to 60 μg of lead usually present in the samples taken for analysis.

The accuracies of the determinations are believed to be about $\pm 1\%$ for the uranium and thorium concentrations and ± 2 to $2\frac{1}{2}\%$ for the concentrations of the lead isotopes. The lead isotope ratios are believed to be accurate to $\pm 1\%$, except that when the 206/204 ratios of the monazite leads approached 1000 the accuracy of the ratio measurement decreased to ± 5 to 10%.

The preparation of the lead samples for spectrometer runs differed from that described by PATTERSON (TILTON *et al.*, 1955) and will be given here. The final dried lead residues were

dissolved in 1 to 2 ml of 2% nitric acid. The pH was adjusted to 4·5 with dilute ammonium hydroxide, using narrow-range pH paper as indicator. The solution was warmed, hydrogen sulphide was bubbled in, and the resulting lead-sulphide precipitate centrifuged down. Part of the precipitate was transferred to an outgassed tantalum ribbon filament, using a portion of the supernate to make a slurry. As the deposit approached dryness (in air) the temperature of the ribbon was increased sufficiently to decompose the ammonium nitrate present from the neutralization step. This presumably converted the lead sulphide to lead sulphate. After the destruction of ammonium nitrate was complete, the samples were loaded into the mass spectrometer where stable emission of Pb^+ peaks by surface ionization occurred at about 750°C. Pure lead sulphide loaded without ammonium nitrate gave inferior runs. This method seems to give better intensities than the method of Patterson, which uses a borax flux on tungsten ribbon which is not outgassed. In addition, no hydrocarbon peaks were noted in the region of the lead spectra with the lead sulphide procedure, while a small hydrocarbon background was present when the borax-tungsten ribbon method was used.

The mass spectrometer used in this work was the Department of Terrestrial Magnetism 60°, 6-in. radius of curvature, Nier-type instrument, equipped with an electron multiplier, which increased the collected ion intensities by a factor of 10^4 to 10^5. The electron multiplier was essential to the lead runs, since lead did not give intense ion beams at the low temperatures at which it was volatilized from the filament.

Results

Age Results

The results of the analyses are given in Table 1. The primary lead corrections for the Houtenbek, Goodhouse, and Steenkampskraal monazites were estimated from the isotopic composition of an average 1000-million-year-old galena, taken from the data of Collins, Russell, and Farquhar (1953), since no local sample was available. We are indebted to Dr. J. W. Graham of the Department of Terrestrial Magnetism for a determination of the isotopic composition of lead in the microcline of the Brown Derby pegmatite. His results were used for the primary lead correction at this site.

Table 1. Monazite age data

Analytical errors of ages are 3 to 5% unless otherwise indicated. Uncertainties in isotopic compositions are mean deviations of 10 to 14 sets of ratios.

Goodhouse Monazite

U: 0·2146 ± 0·0025%, Th: 8·33 ± 0·08%, Pb: 0·3770%

Lead data	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic composition (moles)	0·189 ± 0·010	100·0	9·48 ± 0·10	1151 ± 11
Concentration (p.p.m.)	0·547 ± 0·030	293 ± 6	27·9 ± 0·7	3448 ± 85
Primary lead (assumed)	1·00	16·8	15·50	36·1
Radiogenic lead (p.p.m.)	0	285	19·3	3428
	U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th/Pb^{208}
Age in million years	930	915	880 ± 60	900

Table 1 (*continued*)

Houtenbek Monazite

U: 0·4481 ± 0·0051%, Th: 11·00 ± 0·12%, Pb: 0·5800%

Lead data	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic composition (moles)	0·108 ± 0·008	100·0	8·475 ± 0·09	499·2 ± 5
Concentration (p.p.m.)	1·01 ± 0·08	945 ± 19	80·4 ± 2·0	4777 ± 120
Primary lead (assumed)	1·00	16·8	15·50	36·1
Radiogenic lead (p.p.m.)	0	927	64·5	4740
	U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th/Pb^{208}
Age in million years	1400	1230	930 ± 50	940

Brown Derby Monazite

U: 0·1415 ± 0·0015%, Th: 4·93 ± 0·05%, Pb: 0·2635%

Lead data	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic composition (moles)	0·099 ± 0·005	100·0	9·20 ± 0·09	659 ± 6
Concentration (p.p.m.)	0·336 ± 0·017	343 ± 7	31·7 ± 0·8	2260 ± 57
Primary lead (measured)	1·00	16·72	15·30	35·73
Radiogenic lead (p.p.m.)	0	337	26·4	2250
	U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th/Pb^{208}
Age in million years	1590	1420	1170	995

Steenkampskraal Monazite

U: 0·1102 ± 0·0022%, Th: 5·85 ± 0·06%, Pb: 0·3040%

Lead data	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic composition (moles)	1·29 ± 0·04	100·0	26·6 ± 0·5	1232 ± 15
Concentration (p.p.m.)	2·84 ± 0·09	222 ± 4	59·4 ± 1·5	2760 ± 70
Primary lead (assumed)	1.00	16·8	15·5	36·1
Radiogenic lead (p.p.m.)	0	173	ca. 15	2650
	U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th/Pb^{208}
Age in million years	1080	—	—	990

The constants used in the age calculations in Table 1 were:

U^{238}: $\lambda = 1{\cdot}54 \times 10^{-10}\ yr^{-1}$ (Kovarik and Adams, 1955).

U^{235}: $\lambda = 9{\cdot}72 \times 10^{-10}\ yr^{-1}$ (Fleming, Ghiorso, and Cunningham, 1952).

Th^{232}: $\lambda = 4{\cdot}99 \times 10^{-11}\ yr^{-1}$ (Kovarik and Adams, 1938).

$U^{238}/U^{235} = 137{\cdot}8$ (Inghram, 1946).

As a result of the serious age discrepancies at Brown Derby and Houtenbek, some acid-wash experiments were conducted on the monazites which are described in the following section. The discussion of the adopted ages will be deferred until after the results of the acid-wash experiments have been given.

Results of Acid-wash Experiments

Three of the powdered monazites were treated in cold 6 M hydrochloric acid for 15 min, and the resulting solutions were analysed for uranium, thorium, and lead. The powdered starting materials were finer than 60-mesh and contained about 10% fines, i.e. grains which would not settle in water in 10 sec. The results of the acid-wash experiments, expressed as fractions of the bulk monazite treated, are given in Tables 2 and 3.

Table 2. Isotopic composition of leads in total samples and in acid washes

Sample	Fraction	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}	Radiogenic 208/206
Houtenbek	Total sample	924	78·3	4610	5·04
	Acid soluble	7000	526	1530	0·22
Brown Derby	Total sample	1010	92·9	6660	6·67
	Acid soluble	82·3	18·4	185	2·27
Goodhouse	Total sample	530	50·2	6100	11·8
	Acid soluble	189	26·7	1640	9·3
Steenkampskraal	Total sample	77·3	20·6	952	15·1
	Acid soluble	44·5	16·7	410	13·5

The Houtenbek and Brown Derby monazites have uranium/lead ages considerably in excess of the lead/lead age. The Goodhouse monazite shows good agreement between the uranium/lead, thorium/lead, and lead/lead ages. In the absence of data for the isotopic composition of the primary lead at Steenkampskraal, it is impossible to calculate reliable U^{235}/Pb^{207} and Pb^{207}/Pb^{206} ages for this sample; it is clear that $>75\%$ of the Pb^{207} is nonradiogenic in the specimen.

An interesting correlation between these age measurements and the results of the acid-washing experiments is apparent in Tables 2 and 3. The Houtenbek and Brown Derby monazites contain substantial excesses of acid-soluble uranium

Table 3. Results of acid-wash experiments

Sample		U	Th	Total Pb	Radiogenic		
					Pb^{206}	Pb^{207}	Pb^{208}
Houtenbek	Total sample (p.p.m.)	4481	110,000	5803	927	64·5	4740
	Acid soluble (p.p.m.)	329	1980	278	214	16·1	47·5
	Per cent soluble	7·3	1·8	4·8	23·1	25·0	1·0
Brown Derby	Total sample (p.p.m.)	1415	49,300	2635	337	26·4	2250
	Acid soluble (p.p.m.)	73	1400	45	10·1	0·46	23·4
	Per cent soluble	5·2	2·8	1·7	3·0	1·7	1·0
Goodhouse	Total sample (p.p.m.)	2146	83,300	3770	285	19·3	3430
	Acid soluble (p.p.m.)	44	1390	52	4·77	0·31	44·6
	Per cent soluble	2·0	1·7	1·4	1·7	1·6	1·3

relative to thorium, compared with the amounts of these elements in the bulk powders, while the Goodhouse monazite contains only a small excess of soluble uranium over thorium. This same pattern is reflected in the isotopic composition of the dissolved leads. The Houtenbek and Brown Derby acid-soluble fractions contain excess radiogenic Pb^{206} over radiogenic Pb^{208} compared with the relative abundances of these isotopes in the bulk powders. These isotopes are dissolved from the Goodhouse (and Steenkampskraal) monazites in more nearly the same proportion in which they are present in the bulk powders. In other words, the Goodhouse monazite appears more uniform with regard to the distribution of uranium, thorium, and their respective lead daughters than do the Houtenbek and Brown Derby monazites.

Table 4. Radiogenic (Pb^{207}/Pb^{206}) ratios of leads in acid washes and in total samples

Monazite	Total sample	Acid soluble
Houtenbek	0·0692 ± 0·002	0·0732 ± 0·001
Brown Derby	0·0779 ± 0·002	0·047 ± 0·003
Goodhouse	0·0676 ± 0·002	0·0651 ± 0·002

Interesting differences have been found in the ratios of radiogenic Pb^{207} to radiogenic Pb^{206} in the acid-soluble leads. Table 4 compares these ratios for the soluble leads with those in the total samples. It is not possible to translate the ratios in the acid-soluble phases into Pb^{207}/Pb^{206} ages which have any significance, since we do not know the associations of these leads with uranium in the past.

To interpret the Pb^{207}/Pb^{206} ratios of the soluble leads it would be necessary to know the times during which given amounts of uranium and lead appeared in the soluble phase, the isotopic composition of any pre-existing lead in the phase, and the results of chemical fractionations of uranium and lead which may have occurred in the soluble phase. These same problems are present in determining the Pb^{207}/Pb^{206} age of any mineral, but certain simplified assumptions regarding them are more justifiable for a mineral than for a chemically unstable environment such as the acid-soluble phases of monazites. There are many mathematically possible mechanisms which explain the radiogenic Pb^{207}/Pb^{206} ratios observed in the acid-soluble phases.

The radiogenic (Pb^{207}/Pb^{206}) ratio of the soluble lead in the Brown Derby monazite is one which would normally be associated with a young lead—of the order of 100 million years in age—and the acid-wash data can be explained as the result of the removal of uranium from the mineral in relatively recent times with the resultant deposition of some of its lead in less stable environments. However, the data do not necessitate that all or any part of the soluble lead is 100 million years old, and they do not exclude the possibility that leads with greater ages have been removed from the monazite at times in the past and transported away from the immediate environment of the crystals.

The soluble lead in the Houtenbek monazite appears to be an old lead. If this lead has been removed from its uranium parent only recently and no previous chemical fractionations of uranium and lead occurred in the source material, its Pb^{207}/Pb^{206} age is 1050 million years. It is not necessary that the lead actually be so old, since the bulk monazite itself possessed lead with a radiogenic (Pb^{207}/Pb^{206}) ratio of 0·0732 about 150 million years ago. If the lead was extracted from the monazite at this time, it would appear "older" now, because it was removed from its uranium parent at a time in the past when the U^{235}/U^{238} ratio was larger than it is to-day. There is also a possibility that some of the soluble lead and uranium in the Houtenbek monazite was generated by the decomposition of other monazites in the vicinity of the analysed crystal.

It will also be noted that the 206/204, 207/204, and 208/204 ratios vary between the leads in the total samples and in the acid-soluble fractions of the monazites. The primary lead in the Goodhouse, Brown Derby, and Steenkampskraal samples is more susceptible to removal by acid than the radiogenic lead. In the case of Houtenbek, primary Pb^{208} is more soluble than radiogenic Pb^{208}, but the opposite is true for Pb^{206} and Pb^{207}. These data indicate that the primary and radiogenic leads are not bound with equal stability. Possible explanations are that the primary lead was originally distributed in defect regions, cracks, and fissures, and has remained there, or that it has been transported into the environment of the crystals from some outside source. The data in Tables 2 and 3 demonstrate an inhomogeneous distribution of uranium and thorium in the analysed materials, but it is impossible to decide whether most of this inhomogeneity is derived from the primary crystallization of the monazite or from subsequent alterations which have affected the crystals.

Since these conclusions rest on so few observations, they are admittedly tentative. However, the present acid-wash data do serve to indicate that the

uranium/lead ages are unreliable at Houtenbek and Brown Derby, and that they are more reliable at Goodhouse. Finally, it should be noted that the acid-wash experiments are significant only in so far as they indicate trends. No systematic study such as observing variations of the solubility phenomena over a range of grain size, leach solutions, and temperatures has been attempted.

Discussion

For comparison with present results, all isotopically controlled monazite age determinations published by other investigators are summarized in Table 5. Two

Table 5. Results of other investigators

Monazite	Reference	Age in million years			
		U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th^{232}/Pb^{208}
Ebonite Claims, Southern Rhodesia	Holmes, 1954	2640 2620	2670 2620	2700 2620	2640 2640
Jack Tin Claims, Southern Rhodesia	Holmes, 1954	2210	2460	2660	1940
Irumi Hills, Northern Rhodesia	Holmes, 1954	1990	2330	2640	1380
Antsirabe, Madagascar	Holmes and Cahen, 1955	1370	1850	2450	610
Yadiur, India	Holmes, 1955	1410	1820	2330	1800
Soniana, India	Holmes *et al.* 1949	635	697	913	611
Huron Claim, Manitoba	Nier *et al.* 1941	3180	2840	2600	1830
Las Vegas, New Mexico	Nier *et al.* 1941	1730	1560	1340	770
Mount Isa, Australia	Nier *et al.* 1941	—	—	1160	1000

ages are given for the Ebonite Claims monazite, one assuming no Pb^{204} in the sample and the second assuming that Pb^{204} was equal to the upper limit set in the mass spectrometric analysis. The ages in this table have been recalculated using a value of $7{\cdot}13 \times 10^8$ years for the half-life of U^{235} rather than the value of $7{\cdot}07 \times 10^8$ years which was used in the original papers, This was done solely for the sake of consistency, for the existing information does not permit a real choice between the two values. While two of the monazites have uranium/lead ages which are greater than their respective Pb^{207}/Pb^{206} ages, five others exhibit the reverse type of discrepancy in which the uranium/lead ages are less than the Pb^{207}/Pb^{206} ages. It seems very likely that the Huron Claim and Las Vegas monazites represent cases which are similar to the Houtenbek and Brown Derby monazites of this study, and that acid-wash experiments on these samples would show excesses of soluble uranium and Pb^{206}. Further evidence that the uranium age of the Huron Claim monazite is too high is the fact that uraninite from this site, also studied by Nier,

gives a Pb^{207}/Pb^{206} age of 2600 million years, with lower uranium/lead ages in this instance. In the case of the two Southern Rhodesian monazites, there is geological evidence which indicates that the two post-Bulawayan host pegmatites have approximately the same age. It appears possible to make a twofold classification of "discrepant" monazites, with their uranium/lead ages respectively greater or less than their true ages.

Probable ages of the monazites of this study:

Goodhouse. This monazite appears to be a favourable case similar to that of the Ebonite Claims sample. The acid-wash data indicate no recent uranium-lead fractionation, and the age of this mineral is 900 $\pm$ 50 million years.

Steenkampskraal. In the absence of reliable data concerning the radiogenic Pb^{207} content of the sample, it is difficult to assign an age. Since the data on the acid-soluble lead indicate little recent uranium fractionation, the mineral probably has an age greater than 990 $\pm$ 50 million years and less than 1080 $\pm$ 50 million years.

Houtenbek. The agreement of the thorium/lead and the lead/lead ages at 930 and 940 million years is believed to give a reliable age for this monazite. When uranium/lead and thorium/lead ages are low, as at Jack Tin Claims and Irumi Hills, the thorium/lead age is lowered more than the uranium/lead age, which in turn is lowered more than the lead/lead age. This is an age pattern frequently encountered in other minerals, for example zircon (Tilton and Aldrich, 1955), uraninite (Nier, 1939), titanite (Tilton *et al.*, 1955), apatite (Patterson and Tilton, unpublished), and others. The authors know of only one instance in the literature where a mineral has given a high thorium/lead age. This is the Bisundi uraninite, with an age of 735 million years by uranium/lead and lead/lead and a thorium/lead age of 935 million years (Holmes, Leland, Nier, and Smales, 1949). No monazite has been found as yet which would appear to have a high thorium/lead age where comparisons against other analyses can be made. We may thus consider the thorium/lead age at Houtenbek as a minimum age. If the thorium/lead age for this sample were low, the lead/lead age should have been higher and the removal of uranium observed in the acid-wash experiment would tend to increase it still more with respect to the thorium/lead age. Since no thorium/lead-lead/lead age discrepancy is found, the age of the mineral appears to be 935 $\pm$ 50 million years.

Brown Derby. The Brown Derby monazite determination was part of a larger programme of age determinations on this pegmatite carried out by the group at the Carnegie Institution of Washington. The programme included age determinations by rubidium/strontium and potassium/argon methods as well as additional uranium/lead work. The results indicate an age of 1375 $\pm$ 100 million years for the pegmatite in general. Briefly, microlite gave a Pb^{207}/Pb^{206} age of 1350 million years with a U^{238}/Pb^{206} age of 915 million years, and columbite-tantalite gave a Pb^{207}/Pb^{206} age of 1390 million years with a U^{238}/Pb^{206} age of 1520 million years. The rubidium/strontium and potassium/argon work on micas from the pegmatite are consistent with an age of about 1375 million years. The details of this work will appear shortly in another publication.

There are many interpretations of the chemical history of this monazite which can account for the measured age pattern. One example will suffice as an illustration: The monazite suffered a severe loss of lead at some period in its history, either by a catastrophic loss or through a slow diffusion process; this drastically lowered the Pb^{207}/Pb^{206} age and lowered the uranium/lead and thorium/lead ages even more. In recent times uranium has been removed from the monazite in an amount sufficient to increase the U^{238}/Pb^{206} age to 1590 million years.

It is apparent that in this case the exact meaning of the term "age" becomes somewhat ambiguous. The chemical constituents of the monazite were probably emplaced in the pegmatite 1375 $\pm$ 100 million years ago. However, if the monazite lost substantial amounts (or perhaps even all) of its lead 1000 to 1200 million years ago, some question arises as to whether the "age" of the mineral is actually 1375 million years. The problem obviously depends on the conditions required to produce the lead loss, of which nothing is known. It seems probable that identical past histories (temperature, pressure, ground-water leaching, etc.) will produce different effects on different minerals in the same assemblage and that, as work in age determination progresses, it will have to attempt to take these factors into consideration.

Interpretation of Age Discrepancies

Uranium/Lead Ages Less Than Lead/Lead Age

When uranium/lead and thorium/lead ages are low, the possible causes are lead loss or uranium and thorium gain. Radon leakage may be excluded for two reasons: (1) In the case of the Yadiur monazite, R. D. Connor (see Holmes, 1955, p. 86) found no appreciable loss either from a small crystal or from the powdered monazite. (2) None of the lead/lead ages for these monazites has been demonstrated to be too high, and there is evidence in some instances that they are the more nearly correct of the measured ages.

Although lead loss rather than parent gain is commonly stated to be the cause of low uranium/lead and thorium/lead ages, the authors know of no case for which this has actually been proven. Hecht and Kroupa (1937), Bakken and Gleditsch (1938), Alter and Yuill (1937) have made analyses on layers in single uraninite crystals and have found that the ratio Pb/(U + 0·36 Th) tends to decrease slightly going from the cores to the outer layers, but careful scrutiny of their data fails to provide convincing evidence that the results are caused by loss of lead, nor do any of the authors emphasize this claim in their papers. Considerable difficulty arises in interpreting these experiments, because the initial radial distribution of uranium in the crystals is unknown. It should be noted that an error occurs in data given by Hecht and Kroupa (1937) in which the Pb/(U + 0·36 Th) ratio is stated to be higher for the core of the crystal than for the next two layers. From the uranium, thorium, and lead concentrations listed it is calculated that the ratio is lower for the core than for the surrounding layers.

It can be shown mathematically that the effect on the uranium/lead-lead/lead age pattern is exactly the same for the loss of any given percentage of radiogenic Pb^{206} and radiogenic Pb^{207} at any given time as it would be for the gain of the same

percentage of uranium at the same time. Thus the age pattern in itself is no *definitive* criterion for lead loss. We feel, as do other authors, that lead loss is a more plausible explanation for low uranium/lead and thorium/lead ages than uranium and thorium gain, but it is very difficult to give a definite proof for this hypothesis.

Uranium/Lead Ages Higher Than Lead/Lead Age

The high uranium/lead ages require that there has been a relatively recent loss of uranium, or else an addition of radiogenic Pb^{206} and Pb^{207}. Inspection of the analytical data for the monazite age determinations given in Table 1 and Table 5 indicates that monazite will rarely incorporate more than 120 parts per million of primary lead. (The incorporation of 200 p.p.m. primary Pb in the Steenkampskraal sample is believed to be due to the presence of the titanomagnetite.) In view of the fact that the excess of radiogenic Pb^{206} alone is between 200 and 250 p.p.m. in the case of the Houtenbek and Huron Claim monazites, it is unlikely that the monazite structures will be able to incorporate additional lead to the extent required.

At the Brown Derby site additional work has been done which provides strong evidence that the acid-soluble materials found in the monazite have been derived from the monazite rather than from an outside source. It was stated earlier that this monazite occurred with columbite-tantalite in a matrix of albite-quartz. A single crystal of columbite-tantalite which was located within 2 cm of several large monazite crystals was analysed for the isotopic composition of the lead in its acid-soluble phase. A comparison of this lead and that of the monazite is given in Table 6. It is seen that the soluble leads retain the characteristics of

Table 6. Comparison of leads in two minerals from the Brown Derby pegmatite

Mineral	Source	μg/g acid-soluble lead	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}	Radiogenic 208/206
Monazite	Total sample	45	1010	92·9	6660	6·67
	Acid soluble		82·3	18·4	185	2·27
Columbite-tantalite	Total sample	105	122·7	24·50	55·77	0·19
	Acid soluble		85·6	22·4	57·3	0·31

their respective host minerals in spite of their close spatial relationship in the pegmatite. This result would hardly be expected if the soluble leads were derived from some common external source. A more generalized discussion of the significance of the acid-solubility phenomena to age determination will be given in a separate paper (Tilton, 1956).

From all the information assembled on the monazites reported in this paper, no correlations have been noted which would predict whether the samples would

give good or poor ages *before* the actual analyses were made. There is no correlation of the age results with uranium or thorium contents or with the thorium/uranium ratios of the samples. This does not preclude the possibility that correlations with the bulk chemical composition might be found if such information existed. There is no correlation with microscopic evidence, since, as mentioned earlier, the Brown Derby monazite appeared to be as fresh as the Goodhouse monazite. One possible approach remains for further investigation. The cracks and fissures of the Houtenbek monazite were frequently filled with an orange-brown material, and those of the Brown Derby monazite with an orange-brown material and occasionally with a yellowish material. In contrast, there appeared to be no filling in the cracks and fissures of the Goodhouse monazite. Radioautograph studies were made by stripping-film techniques on two thin sections each of the Brown Derby and Goodhouse monazites. These studies showed no noticeable enrichment of radioelements in the cracks of either monazite, but the possibility remains that the filling of the cracks bears some relationship to the process or processes which altered the age results at Brown Derby and Houtenbek. A criterion which would permit evaluation of the age results before the analyses were attempted would obviously be of great value in monazite age work.

Summary

The acid-wash experiments appear to indicate the trend of recent alterations affecting the uranium, thorium, and lead contents of the monazites, and they correlate strikingly with certain features of the age pattern. Interesting differences were found in the radiogenic (Pb^{207}/Pb^{206}) ratios of the acid-soluble leads, but it is not possible to interpret these observations with any high degree of certainty. There were marked differences in the solubilities of the primary and radiogenic leads of the monazites.

It is apparent that monazites often exhibit fractionation of uranium, thorium, and lead. Very little is understood regarding the mechanisms by which these fractionations occur, and it is necessary to assemble complete age data on a monazite in order to detect fractionation.

Acknowledgements—We should like to express our appreciation to our colleagues, G. W. Wetherill, G. L. Davis, and L. T. Aldrich, of the Carnegie Institution of Washington, for constructive discussions and criticisms of this work. We are particularly indebted to L. T. Aldrich and J. B. Doak, who were responsible for the construction and maintenance of the mass spectrometer at the Department of Terrestrial Magnetism. The enriched U^{235} tracer was provided by the Isotopes Division of the Oak Ridge National Laboratory.

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Solid diffusion in radioactive minerals and the measurement of absolute age

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(*Received* 23 *March* 1956)

Abstract—Diffusion of the daughter products of radioactive decay schemes from a mineral will be manifested in a pattern of discrepant age measurements. The theory of daughter product diffusion is examined in detail, and developed in graphical form. U, Th-bearing minerals frequently exhibit the discrepant pattern Pb^{207}/Pb^{206} age > Pb^{207}/U^{238} age > Pb^{206}/U^{238} age, which may be explained by diffusion; with this assumption, use of the graphs given in this paper will indicate the true age of the mineral and the diffusion coefficient which governed the loss of Pb. Examples of such graphical application of diffusion theory are given for several zircon concentrates and monazite samples, and values of the Pb diffusion coefficient between 10^{-21} cm²/sec and 10^{-23} cm²/sec are obtained.

The effects of isotopic mass, daughter product concentration, radiation damage, and temperature are discussed; it is concluded that daughter product diffusion deserves consideration that daughter product diffusion deserves consideration as a *possible* cause of discrepant age measurements, obtained from the use of several decay schemes. This theory of daughter isotope diffusion can be tested quantitatively by performing age determinations on several mineral samples (possessing a large variation in grain size) from a particular locality.

An important part of the study of geologic time deals with the relationship between the several ages that may be calculated for a particular radioactive mineral, using each of the radioactive decay schemes available. In the case of uranium- and thorium-bearing minerals, independent calculations may be made in respect of the decay schemes $U^{238} \rightarrow Pb^{206}$, $U^{235} \rightarrow Pb^{207}$, and $Th^{232} \rightarrow Pb^{208}$; for a muscovite, lepidolite or potassium feldspar, one may frequently use the decay schemes $Rb^{87} \rightarrow Sr^{87}$ and $K^{40} \rightarrow A^{40}$. Since the studies of Nier (1939, 1941), workers in this field have been faced with a challenging problem in that there are many more examples of single minerals yielding discrepant results than there are of good agreement between the several decay schemes. This is clearly demonstrated in the age-measurement tables compiled by Faul *et al.* (1954, pp. 262–280). The discrepancies are frequently greater than the combined uncertainties in the nuclear decay constants, mass spectrometry, and chemical determinations.

The use of stable-isotope dilution techniques has permitted the determination of apparent ages of zircon and mica coexisting in several Pre-Cambrian granites, using several decay schemes (Aldrich, Tilton, Davis, Nicolaysen, and Patterson 1955; Tilton and Aldrich, 1955). In certain cases these authors were able to determine the apparent ages of lepidolites in pegmatites related to the above-mentioned granites, using the $Rb^{87} \rightarrow Sr^{87}$ decay scheme. Here too the several calculated ages reveal wide discrepancies, which are considerably in excess of the uncertainties involved in making the individual age determinations. Some of the data obtained by Tilton and co-workers on granite zircons are summarized in Table 1.

Table 1.

Locality	Source	Age in millions of years			
		U^{238}/Pb^{206}	U^{235}/Pb^{207}	Pb^{207}/Pb^{206}	Th^{232}/Pb^{208}
Cape Town, S. Africa	Granite	330	354	525	237
Tory Hill, Ontario	Granite	1020	1050	1110*	390
Bagdad, Arizona	Granite	630	770	1210	270
Gunnison, Colorado	Granite	930	1130	1540*	515

* Corrected values.

Aldrich *et al.* (1955, p. 12) have discussed the possible causes of the disagreement between the calculated ages. It has become obvious that an understanding of the nature of the discrepancies in the ages of the zircons alone is needed, in order to draw a reliable conclusion about the wider pattern, embracing the $Rb^{87} \rightarrow Sr^{87}$ decay scheme. The same authors have dealt quantitatively with two possible causes of the disagreement in zircon age measurements, radon leakage, and a recent "catastrophic" loss of lead. The purpose of this communication is to discuss a third possible cause of the discrepancies—a slow loss of lead by diffusion from the zircons—using the classical theory of diffusion in solids.

The theory is also applied to monazites, in order to investigate the possible importance of solid diffusion in bringing about a type of discrepant pattern frequently observed in this mineral. The results of many age measurements on monazite are summarized by Tilton and Nicolaysen (1956).

Theory of Diffusion in a Radioactive Mineral

The fundamental reason why solid diffusion can be expected to play a finite role in altering the composition of any mineral lies in the atomic vibration and agitation which has been imposed on the mineral structure throughout its thermal history. Accompanying this motion is a continual movement of lattice dislocations, structural holes, and impurity atoms, striving to maintain minimal free-energy states. Over geological periods of time (i.e. $\sim 10^8$ years) one will therefore expect a certain random movement of both radioactive elements and their daughter products. Such random motion can be interpreted in terms of a flow of the diffusing atoms, which is proportional to the negative gradient of their partial molal free energy. Mathematically expressed, the diffusion flux of atoms of the daughter element is

$$U = -D \operatorname{grad} \bar{G}_z \tag{1}$$

where D = the diffusion coefficient,

$\bar{G}_z$ = the partial molal free energy of the daughter element in the mineral considered.

In the following treatment we shall consider only the diffusion of the daughter product of a radioactive decay scheme, neglecting the diffusion of the parent element. It is assumed that the diffusion coefficient of the daughter element is much greater than the diffusion coefficient of the radioactive element, throughout the history of the mineral. Isotopically controlled analyses of fresh uranium- and thorium-bearing minerals such as zircon and monazite usually show extremely small amounts of primary lead.

For example, TILTON *et al.* (1955, Table 3) have shown that in the granite from Tory Hill, Ont., the zircons crystallized with the ratio Primary Pb/U $< 1/800$, while the ratio of Pb/U in the granite was approximately 3·0. This is a consequence, at least in part, of a preferential binding of uranium over lead in the zircon structure at the temperature of crystallization. In the case of monazite (Ce, La, Nd, etc.) PO_4, simple ionic radius considerations make it seem plausible that lead will diffuse out of the structure to a greater extent than uranium and thorium. The ionic radii of U^{4+} (0·97 Å) and Th^{4+} (1·20 Å) are rather close to that of Ce^{4+} (0·94 Å), while the ionic radius for Pb^{2+} (1·20 Å) differs enough from that of the rare-earth cation to make lead appear somewhat of a "misfit" in the monazite structure. (This argument assumes that the bonding of Pb in monazite is mainly ionic, in which case the divalent ion is present.)

Further assumptions will be:

(i) At every point the free-energy gradient is equal to the concentration gradient (grad C);

(ii) The atoms of the radioactive element are distributed uniformly within the mineral.

We denote the flux U by $-D$ grad C, and

N = the instantaneous concentration of parent atoms,

N_0 = the initial concentration of parent atoms,

$\lambda N = \lambda N_0 e^{-\lambda t}$ = the unit-time generation of daughter atoms by radioactivity.

If this flux is integrated over a sphere of the mineral and GAUSS's theorem is applied, the time variation of the concentration of the daughter atoms is given by the differential equation

$$\partial C/\partial t = D\nabla^2 C + \lambda N_0 e^{-\lambda t} \tag{2}$$

Adopting the initial and boundary conditions $C = C_0$, $t = 0$, and $C = 0$, all t, $r = a$ (the radius of the mineral sphere), respectively, the equation has the following analytic solution:

$$C/N = -1 + 3/d^2 - 3\cot d/d + 6/\pi^2 \sum_{n=1}^{\infty} e^{\lambda t(1-n^2\pi^2/d^2)}/n^2\left(1 - \frac{n^2\pi^2}{d^2}\right) + \frac{6C_0}{N\pi^2}\sum_{n=1}^{\infty}\frac{e^{-n^2\pi^2 Dt/a^2}}{n^2} \tag{3}$$

where we adopt the substitution $d^2 = \lambda a^2/D$. Some notes concerning this solution, which was stated by WASSERBURG (1954), are given in Appendix 1. ROSENQVIST (1949a) has given an analytic solution for a limiting case, where the age of the mineral is small compared to the half-life of the radioactive element involved.

An important modification must be noted concerning the boundary condition

of zero concentration of the daughter product at the surface of the sphere throughout its history. If we denote

$\bar{G}_M$ = the partial molal free energy of the daughter product in the mineral forming the matrix of the radioactive substance,

$\Delta\bar{G} = \bar{G}_M - \bar{G}_z$,

then the same boundary condition is more effectively expressed by the proviso that $\Delta\bar{G}$ has a negative sign, and has a magnitude very much larger than the activation energy for diffusion of the daughter product in the matrix mineral itself. In mineralogical terms, this means that if a zircon or uraninite crystal is surrounded by a matrix of galena throughout its history, the diffusion of radiogenic lead out of the radioactive mineral *may* still be accurately described by the analytic solution given above, despite the continuous and high concentration of lead at the boundary of the crystal.

In the case of a radioactive mineral containing a negligible amount of primary contamination by the element which forms the daughter product of a particular decay scheme, the last term drops away from the analytic solution. In this case the parameter C/N may be immediately translated into a "measured" or "apparent" age, by substitution in the age equation

$$t_{\text{measured}} = \ln (1 + C/N)/\lambda \tag{4}$$

For each decay scheme (λ constant), a particular value of the true age (t_{true}) will give rise to only one particular value of t_{measured} for each and every positive value of the parameter D/a^2.

Graphical Presentation of the Diffusion Theory

The variation of $\ln (1 + C/N)$ with t_{true} has been accurately computed for twenty-one different values of d^2. The variation of t_{measured} with t_{true} (for each decay scheme) has therefore been calculated in terms of twenty-one different values of the parameter D/a^2. These data are presented graphically for the $U^{238} \rightarrow Pb^{206}$, $U^{235} \rightarrow Pb^{207}$, and $Th^{232} \rightarrow Pb^{208}$ decay schemes in Figs. 1, 2, and 3. By plotting the variation of D/a^2 with t_{measured} in terms of a family of curves representing different values of t_{true} for the decay scheme $U^{238} \rightarrow Pb^{206}$, these curves were used together with Fig. 2 for calculating the variation of "true age" and "measured age" for Pb^{207}/Pb^{206} age calculations (Fig. 4).

Part of the numerical data used for drawing up these graphs is given in Table 2. These figures will facilitate calculation of a similar series of curves relating "measured age" and "true age" for any decay scheme, through division of the values of $\ln (1 + C/N)$ and λt by the appropriate value of the decay constant λ.

The curves in Figs. 1–4 show several features which are relevant to the problem of discrepant age measurements. Taking a particular true age for a U- and Th-bearing mineral, it is simple to interpolate (from each family of curves) the value of the age that will be measured for each decay scheme, assuming one particular value of D to have governed the diffusion of the Pb isotopes.

An example of such interpolation is given in Table 3.

Table 2.

$d^2 = \frac{\lambda a^2}{D}$	Values of ln $(1 + C/N)$ for different values of λt											
	$\lambda t = 0{\cdot}02$	$\lambda t = 0.04$	$\lambda t = 0{\cdot}06$	$\lambda t = 0{\cdot}08$	$\lambda t = 0{\cdot}10$	$\lambda t = 0{\cdot}12$	$\lambda t = 0{\cdot}14$	$\lambda t = 0{\cdot}16$	$\lambda t = 0{\cdot}18$	$\lambda t = 0{\cdot}2$	$\lambda t = 0{\cdot}3$	$\lambda t = 0{\cdot}4$
$0{\cdot}04\pi^2$	0·01139	0·01747	0·02112	0·02336	0·02475	0·02560	0·02613	0·02646	0·02666	0·02678	0·02697	0·02698
$0{\cdot}09\pi^2$	0·01393	0·02368	0·03118	0·03713	0·04192	0·04577	0·04889	0·05143	0·05351	0·05520	0·05998	0·06171
$0{\cdot}16\pi^2$	0·01532	0·02728	0·03733	0·04598	0·05355	0·06020	0·06610	0·07132	0·07603	0·08015	0·09541	0·1043
$0{\cdot}25\pi^2$	0·01620	0·02959	0·04135	0·05190	0·06148	0·07024	0·07830	0·08575	0·09265	0·09906	0·1252	0·1439
$0{\cdot}36\pi^2$	0·01680	0·03120	0·04419	0·05610	0·06716	0·07749	0·08719	0·09633	0·1050	0·1132	0·1485	0·1767
$0{\cdot}49\pi^2$	0·01720	0·03235	0·04624	0·05919	0·07138	0·08291	0·09387	0·1043	0·1143	0·1239	0·1668	0·2030
$0{\cdot}64\pi^2$	0·01757	0·03328	0·04788	0·06163	0·07469	0·08716	0·09911	0·1106	0·1217	0·1324	0·1814	0·2242
$0{\cdot}81\pi^2$	0·01784	0·03400	0·04915	0·06355	0·07731	0·09053	0·1033	0·1156	0·1276	0·1392	0·1931	0·2415
$1{\cdot}21\pi^2$	0·01820	0·03503	0·05102	0·06636	0·08118	0·09554	0·1095	0·1231	0·1364	0·1494	0·2109	0·2677
$1{\cdot}69\pi^2$	0·01848	0·03578	0·05235	0·06838	0·08395	0·09912	0·1140	0·1285	0·1428	0·1568	0·2237	0·2867
$2{\cdot}25\pi^2$	0·01868	0·03633	0·05334	0·06987	0·08600	0·1018	0·1173	0·1325	0·1475	0.1622	0·2333	0·3010
$2{\cdot}89\pi^2$	0·01884	0·03675	0·05412	0·07102	0·08759	0·1038	0·1198	0·1356	0·1511	0·1665	0·2408	0·3121
$6{\cdot}25\pi^2$	0·01920	0·03777	0·05595	0·07383	0·09146	0·1089	0·1261	0·1432	0·1601	0·1769	0·2592	0·3393
$12{\cdot}25\pi^2$	0·01943	0·03840	0·05710	0·07557	0·09386	0·1120	0·1300	0·1479	0·1657	0·1834	0·2706	0·3563
$20{\cdot}25\pi^2$	0·01956	0·03876	0·05773	0·07655	0·09521	0·1138	0·1322	0·1505	0·1688	0·1870	0·2770	0·3659
$30{\cdot}25\pi^2$	0·01987	0·03909	0·05821	0·07719	0·09622	0·1149	0·1334	0·1522	0·1708	0·1893	0·2811	0·3720

$d^2 = \frac{\lambda a^2}{D}$	Values of ln $(1 + C/N)$ for different values of λt											
	$\lambda t = 0{\cdot}5$	$\lambda t = 0{\cdot}6$	$\lambda t = 0{\cdot}7$	$\lambda t = 0{\cdot}8$	$\lambda t = 0{\cdot}9$	$\lambda t = 1{\cdot}0$	$\lambda t = 1{\cdot}5$	$\lambda t = 2{\cdot}0$	$\lambda t = 2{\cdot}5$	$\lambda t = 3{\cdot}0$	$\lambda t = 3{\cdot}5$	$\lambda t = 4{\cdot}0$
$0{\cdot}04\pi^2$	0.02699	0.02699	0·02699	0·02699	0·02699	0·02699	0·02699	0·02699	0·02699	0·02699	0·02699	0·02699
$0{\cdot}09\pi^2$	0·06235	0·06257	0·06266	0·06269	0·06270	0·06270	0·06270	0·06270	0·06270	0·06270	0·06270	0·06270
$0{\cdot}16\pi^2$	0·1095	0·1125	0·1144	0·1154	0·1161	0·1164	0·1169	0·1170	0·1170	0·1170	0·1170	0·1170
$0{\cdot}25\pi^2$	0·1575	0·1675	0·1748	0·1802	0·1842	0·1871	0·1936	0·1950	0·1953	0·1954	0·1954	0·1954
$0{\cdot}36\pi^2$	0·1995	0·2181	0·2334	0·2461	0·2565	0·2652	0·2910	0·3014	0·3056	0·3074	0·3081	0·3084
$0{\cdot}49\pi^2$	0·2341	0·2611	0·2847	0·3055	0·3239	0·3401	0·3980	0·4309	0·4499	0·4610	0·4676	0·4715
$0{\cdot}64\pi^2$	0·2623	0·2967	0·3280	0·3565	0·3827	0·4067	0·5026	0·5693	0·6168	0·6513	0·6765	0·6951
$0{\cdot}81\pi^2$	0·2855	0·3262	0·3640	0·3994	0·4326	0·4639	0·5976	0·7029	0·7880	0·8580	0·9149	0·9642
$1{\cdot}21\pi^2$	0·3210	0·3715	0·4197	0·4659	0·5105	0·5536	0·7522	0·9302	1·093	1·246	1·389	1·524
$1{\cdot}69\pi^2$	0·3467	0·4043	0·4601	0·5144	0·5673	0·6192	0·8666	1·101	1·328	1·550	1·768	1·984
$2{\cdot}25\pi^2$	0·3660	0·4291	0·4906	0·5509	0·6101	0·6685	0·9524	1·229	1·503	1·777	2·051	2·325
$2{\cdot}89\pi^2$	0·3810	0·4483	0·5143	0·5793	0·6434	0·7069	1·018	1·326	1·635	1·946	2·260	2·576
$6{\cdot}25\pi^2$	0·4180	0·4956	0·5725	0·6487	0·7245	0·8001	1·176	1·555	1·938	2·327	2·721	3·120
$12{\cdot}25\pi^2$	0·4410	0·5250	0·6085	0·6916	0·7744	0·8572	1·271	1·688	2·110	2·538	2·970	3·406
$20{\cdot}25\pi^2$	0·4540	0·5415	0·6286	0·7155	0·8023	0·8890	1·323	1·760	2·202	2·648	3·098	3·551
$30{\cdot}25\pi^2$	0·4622	0·5520	0·6415	0·7308	0·8200	0·9092	1·356	1·805	2·259	2·715	3·176	3·640

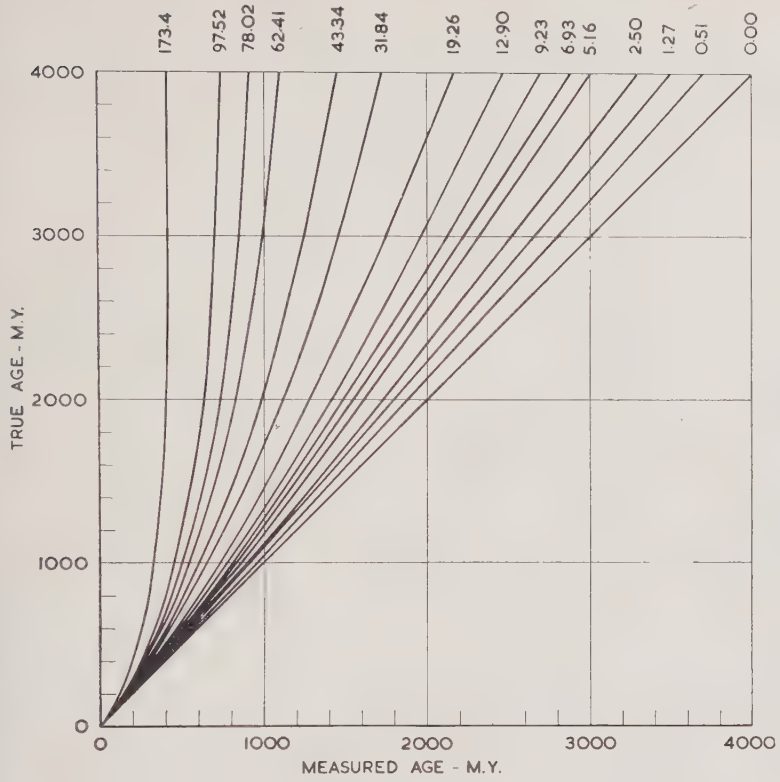

FIG. 1. Variation of true Pb^{206}/U^{238} age and measured Pb^{206}/U^{238} age, for different values of the parameter D/a^2 given in the units 10^{-12} yr^{-1}.

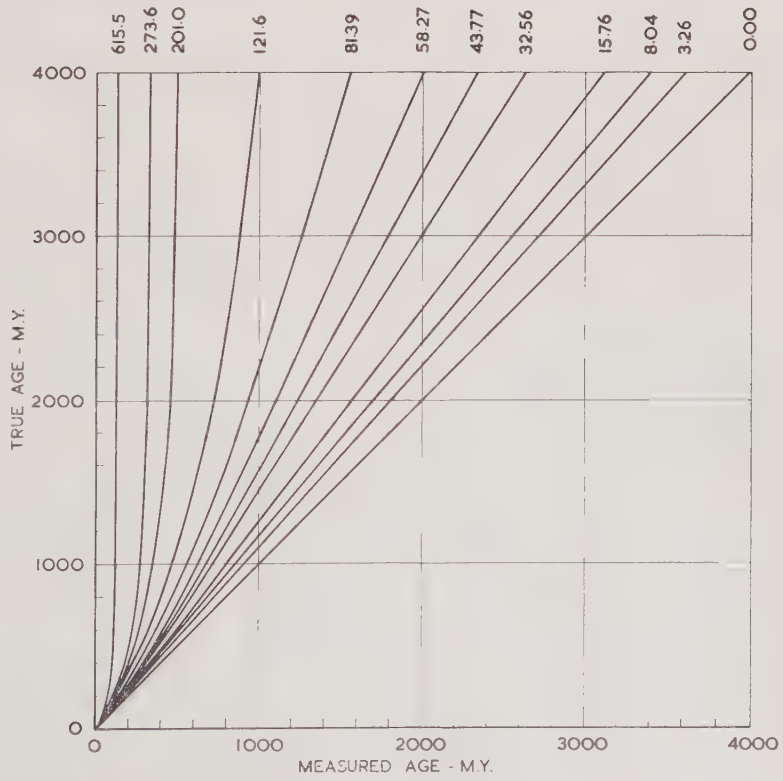

FIG. 2. Variation of true Pb^{207}/U^{235} age and measured Pb^{207}/U^{235} age, for different values of the parameter D/a^2 given in the units 10^{-12} yr^{-1}.

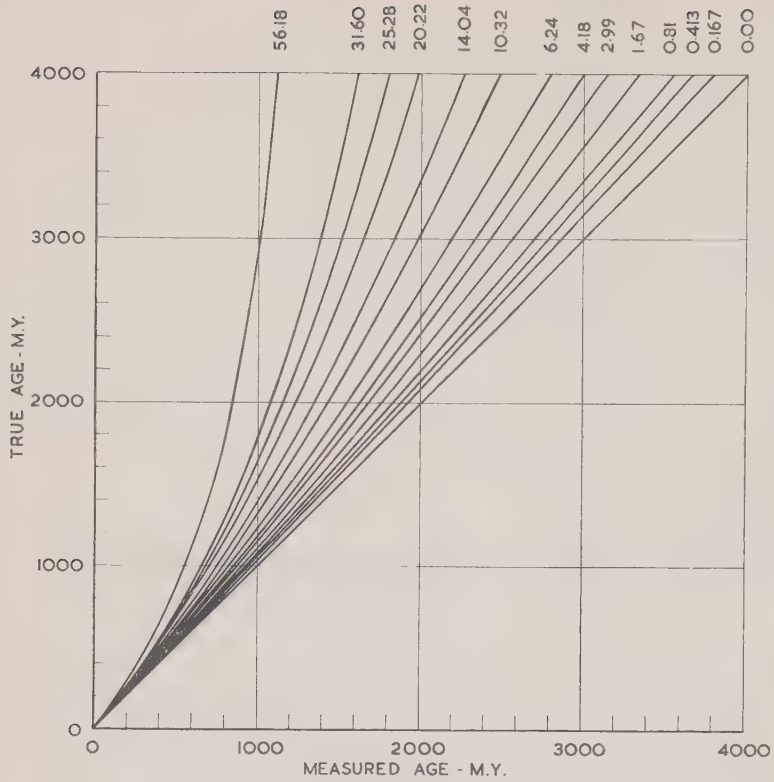

Fig. 3. Variation of true Pb^{208}/Th^{232} age and measured Pb^{208}/Th^{232} age, for different values of the parameter D/a^2 given in the units 10^{-12} yr^{-1}.

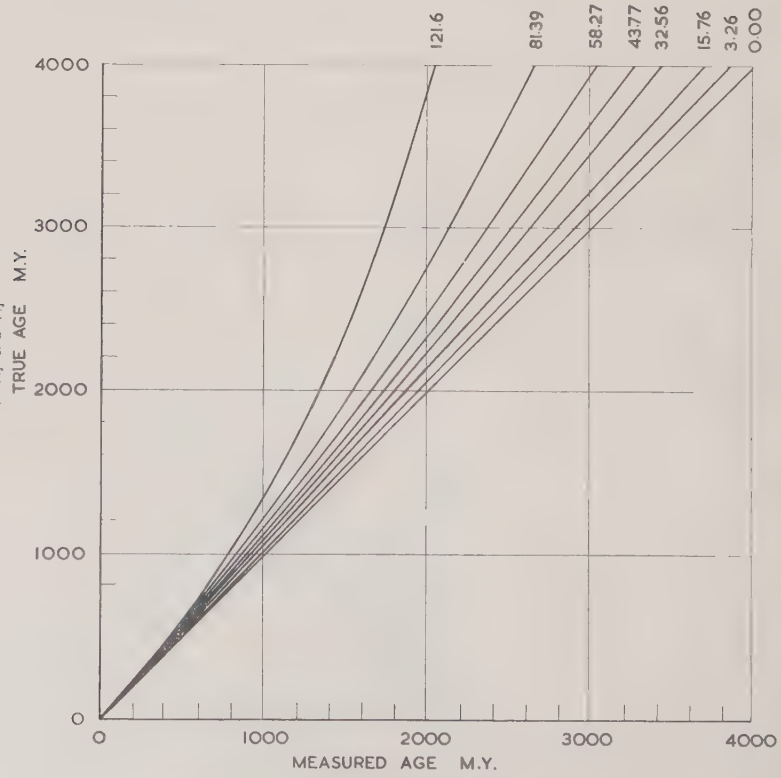

Fig. 4. Variation of true Pb^{207}/Pb^{206} age and measured Pb^{207}/Pb^{206} age, for different values of the parameter D/a^2 given in the units 10^{-12} yr^{-1}.

Table 3. (t_{true} equal to 1000 million years)

Diffusion coefficient	Spherical radius	Measured age (m.y.)			
		Pb^{207}/Pb^{206}	Pb^{207}/U^{235}	Pb^{206}/U^{238}	Pb^{208}/Th^{232}
2×10^{-14} cm^2/year	1/10 cm	991	927	907	904
	0·025 cm	912	714	656	646
10^{-13} cm^2/year	$\frac{1}{2}$ cm	~998	~970	959	957
	1/10 cm	965	843	800	793
	0·025 cm	739	402	348	335
10^{-12} cm^2/year	$\frac{1}{2}$ cm	974	900	870	866
	1/10 cm	816	511	450	440

The "discrepant" pattern which results from lead diffusion in a uranium- and thorium-bearing mineral will always be of the form shown by Table 3, provided that the diffusion has been subject to the assumptions stated at the outset of our treatment. The lowest age is associated with the lowest value of the decay constant (that of Th^{232}), and the sequence of measured ages follows the sequence of values of the decay constant. The Pb^{207}/Pb^{206} age will always be the highest measured age. This is qualitatively the same pattern observed in the comprehensive zircon age measurements mentioned previously.

A quantitative evaluation of the feasibility of Pb diffusion in a U- and Th-bearing mineral may be made by correct use of the curves in Figs. 1–4. A particular value of $t_{measured}$ can be expressed as a series of possible values of t_{true}, each associated with a particular value of D/a^2. For example, the value of $t_{measured}$ for the decay scheme U^{238}/Pb^{206} is 330 million years in the case of a zircon concentrate from the Cape granite, South Africa. By drawing a vertical line in Fig. 1 at the point $t_{measured}$ = 330 million years, one can read off the values of t_{true} where this line intersects each curve representing a different value of D/a^2. These intersections are represented in a smooth curve (giving the functional relation between t_{true} and D/a^2) in Fig. 5. The values of $t_{measured}$ obtained from the ratios Pb^{208}/Th^{232}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206} (237, 354, and 525 million years, respectively) are used in the same way to obtain the curves in Fig. 5. The values of D/a^2 (94×10^{-12} years $^{-1}$) and t_{true} (590 m.y.) where the Pb^{207}, Pb^{206}, and Pb^{207}/Pb^{206} curves intersect in Fig. 5, now deserve consideration in any attempt to explain the differences in the measured ages. If these zircons crystallized 590 million years ago, and a constant diffusion coefficient has governed the loss of lead isotopes throughout the history of the mineral, then the present pattern of "discrepant" lead-uranium and lead-lead ages would result.* In order to establish an order of magnitude for the diffusion constant

* The intersection of any two of these three curves in Fig. 5 is sufficient to establish this particular point. The single intersection point for the three curves merely proves arithmetic consistency in the computations used to make up Figs. 2, 3, and 4.

indicated by this theory, it is only necessary to know the effective spherical radius of the zircon crystals. This is estimated at $\sim 4 \times 10^{-3}$ cm, or $a^2 \sim 16 \times 10^{-6}$ cm^2. The value of D is then 15×10^{-16} cm^2/year, or $\sim 5 \times 10^{-23}$ cm^2/sec. The arithmetic mean of the distances traversed by lead atoms in such zircon crystals over a time t equal to 600 million years is given by

$$X = (2Dt)^{\frac{1}{2}} \tag{5}$$

and here $X \sim 10^{-3}$ cm, or approximately one-sixth of the width of these crystals, which form tetragonal prisms with slender pyramidal terminations.

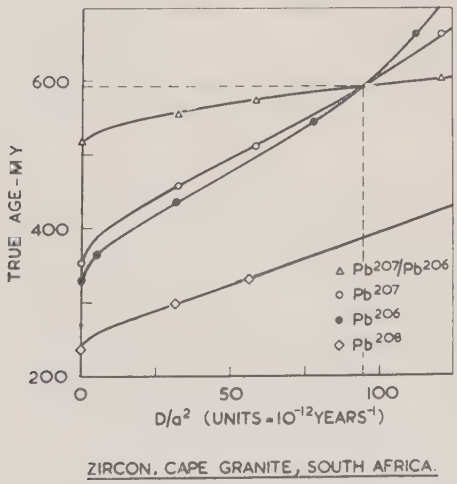

Fig. 5. Variation of true age and the parameter D/a^2, for the zircon concentrate from the Cape granite, South Africa.

Table 4.

Mineral sample (zircon concentrates)	D/a^2 (10^{-12} years^{-1})	t_{true} (m.y.)	Estimated a^2 (cm^2)	Calculated D (cm^2/sec)
Cape granite, S. Africa	94	590	16×10^{-6}	5×10^{-23}
Tory Hill granite, Ont.	2.1	1134	10^{-2}	6×10^{-22}
Bagdad granite, Arizona	78	1490	16×10	4×10^{-23}
Gunnison granite, Colo.	40·6	1760	16×10^{-6}	2×10^{-23}
Monazite samples				
Jack Tin Claims, S. Rhod.	4.3	2760	4×10^{-2}	5×10^{-21}
Irumi Hills. N. Rhod.	8.8	2780		
Antsirabe, Madagascar	32·0	2790	$<3{\cdot}6 \times 10^{-4}$	$<4 \times 10^{-22}$
Yadiur, India	26·2	2605		
Soniana, India	38·4	1016		

The measured ages given in Table 1 for other zircon concentrates from felsic rocks have been analysed in the same manner, and their values of t_{true} as a function of D/a^2 have been plotted in Figs. 6, 7, and 8. Age measurements on five monazite samples given by HOLMES (1949, p. 294; 1954, p. 613; 1955, p. 85)—see also

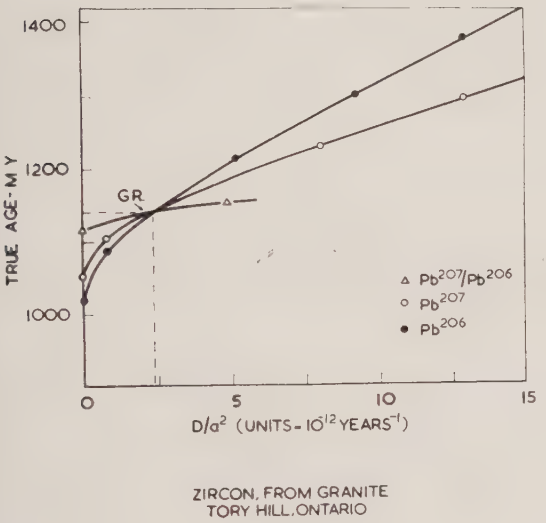

FIG. 6. Variation of true age and the parameter D/a^2, for the zircon concentrate from the Tory Hill granite, Ontario.

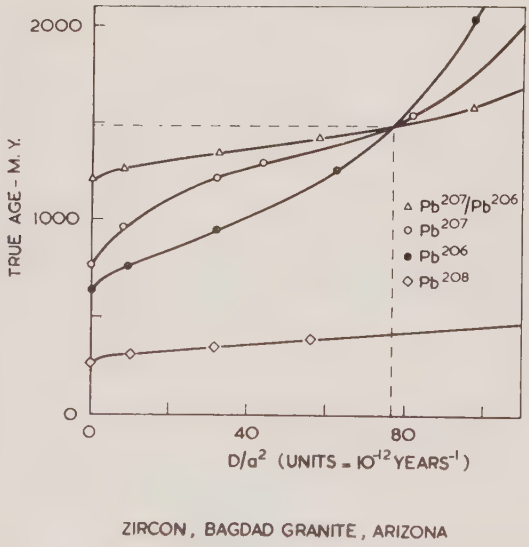

FIG. 7. Variation of true age and the parameter D/a^2, for the zircon concentrate from the Bagdad granite, Arizona.

Table 5 in TILTON and NICOLAYSEN (1956)—have been similarly treated, and these data are plotted in Figs. 9–13. The values of t_{true} and D/a^2 obtained from the intersection points of all these Pb^{206}, Pb^{207}, and Pb^{207}/Pb^{206} curves are given in Table 4; the estimated values of a^2 and resulting calculated values of the diffusion coefficient are also indicated.

Whenever the relationship Pb^{207}/Pb^{206} > age Pb^{207}/U^{235} age > Pb^{206}/U^{238} age occurs, these measurements can quantitatively be reconciled in terms of a lead-diffusion hypothesis, with the "true age" somewhat higher than the measured Pb^{207}/Pb^{206} age. The curves plotted in Figs. 5–13 indicate that this hypothesis does not in general explain the Pb^{208}/Th^{232} age discrepancy; in nearly all cases a

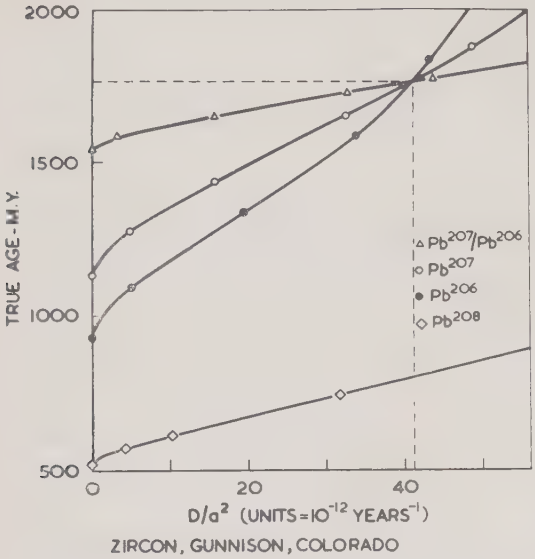

Fig. 8. Variation of true age and the parameter D/a^2, for the zircon concentrate from the Gunnison granite, Brown Derby Colorado.

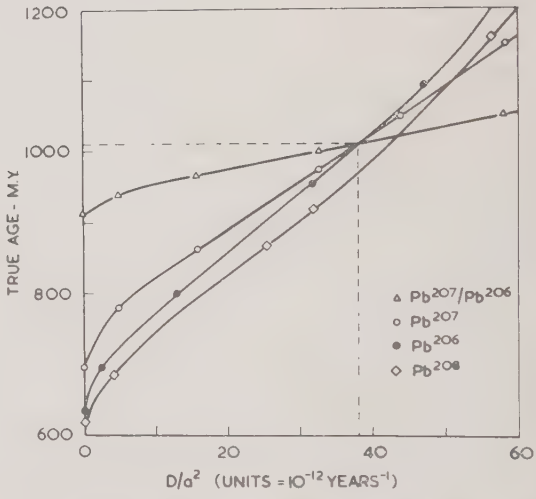

Fig. 9. Variation of true age and the parameter D/a^2, for monazite from Soniana, Mewar State, India.

specifically higher value of D/a^2 would be needed for Pb^{208} in order to bring the Pb^{208}/Th^{232} age into agreement with the "true age" mentioned above. A possible explanation of this anomaly has been suggested by Tilton *et al.* (1955), who postulate a heterogeneous distribution of the uranium and thorium through a large part of the history of the Tory Hill zircons, with a relative concentration of the thorium towards the crystal margins.

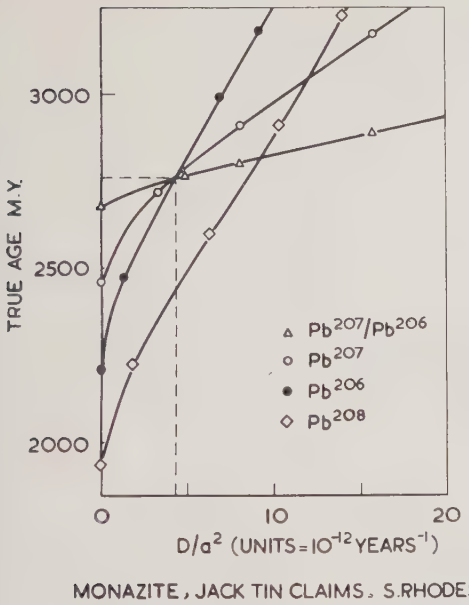

FIG. 10. Variation of true age and the parameter D/a^2, for monazite from Jack Tin Claims, Southern Rhodesia.

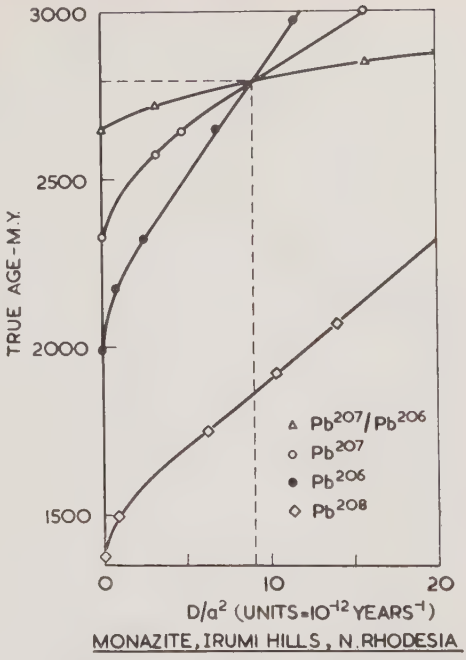

FIG. 11. Variation of true age and the parameter D/a^2, for monazite from Irumi Hills, Northern Rhodesia.

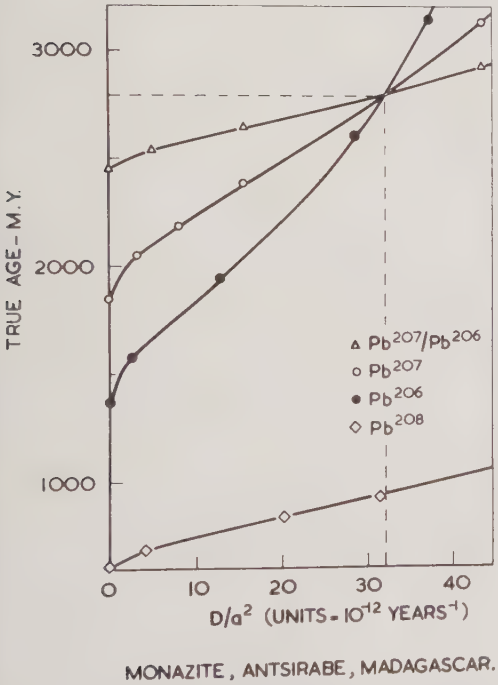

FIG. 12. Variation of true age and the parameter D/a^2, for monazite from Antsirabe, Madagascar.

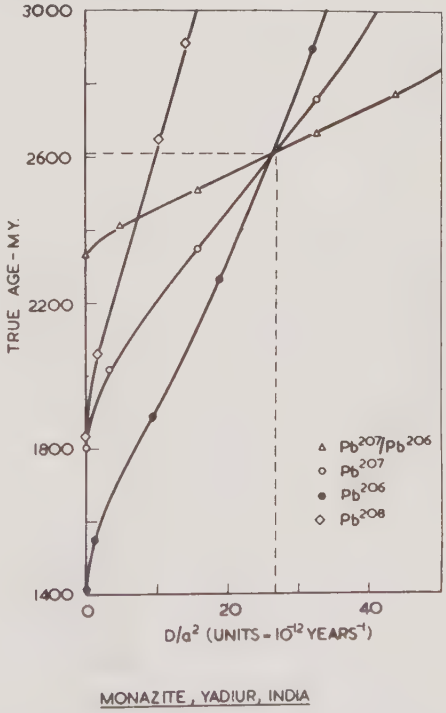

FIG. 13. Variation of true age and the parameter D/a^2, for monazite from Yadiur, India.

Our initial assumption (ii) of a uniform distribution of the radioactive elements within the mineral, was a highly idealized conception. When the difference in chemical properties between U^{4+} and Th^{4+} is taken into account, a nonuniform distribution of these cations in zircon crystals should cause little surprise.

The approximate coincidence of the "true ages" indicated for the three Rhodesian monazites and the Antsirabe sample is of interest in connection with the graphical methods for portraying "convergent" age data, recently discussed by Ahrens (1955 a,b). Detailed discussion is not warranted in the case of the Irumi Hills alluvial monazite, which has a high concentration of primary lead.

The measured age pattern given by the monazite from Soniana (Mewar State, India) is in fairly close agreement with the theory of lead diffusion (see Fig. 9). Three intersections are obtained, with the values of "true age" at 1016, 1022, 1094 million years, accompanied by the parameter D/a^2 at $38{\cdot}4 \times 10^{-12}$, $43{\cdot}3 \times 10^{-12}$, and $50{\cdot}4 \times 10^{-12}$ years^{-1} respectively. Holmes (1949, p. 293) states that the analysed material consists of:

> "large and small fragments of monazite crystals, some of which must have been several inches long" . . .
> "fractured surfaces show evidence of patchy internal decomposition. The fresh-looking portions are yellowish-brown and resinous, but these are veined and surrounded by duller material. Many smaller veinlets and fractures could be seen in thin section. After crushing, the most resinous portions, free from visible veins, were picked out and prepared for the analysis."

A calculation of the value of D would be unjustified in view of this method of selecting the sample. It appears possible that the duller material and the veinlets may contain radiogenic lead which has been lost from the fresh-looking portions of the original material. The value of age measurements embracing several portions of a radioactive mineral and its matrix will be clear from this example.

Effect of Isotopic Mass on the Diffusion Coefficient

In the preceding discussion we have assumed that the diffusion of each lead isotope, Pb^{206}, Pb^{207}, and Pb^{208}, will be determined by only one constant value of the diffusion coefficient D. A quantitative estimate of the effect of the isotopic mass differences can be made through the following considerations: the magnitude of the diffusion constant will be directly related to the frequency with which the particular lead isotope attains an energy sufficient to surmount a potential energy barrier—the energy barrier associated with each elementary "jump" in the diffusion process. This frequency will in turn be related to the spectrum of frequencies governing the vibrational motion in the solid.

The frequency of a simple harmonic motion is given by

$$\nu = 1/2\pi \text{ (restoring force per unit displacement/mass)}^{\frac{1}{2}}.$$

If we consider the lead to be present in such a small proportion that interactions between lead atoms can be neglected, and the "restoring force" term can be regarded as constant, then the diffusion constants will vary in inverse proportion to the square roots of the masses,

i.e. $$D\,Pb^{206}/D\,Pb^{208} = (208/206)^{\frac{1}{2}} = 1{\cdot}0048.$$

Where the proportion of lead becomes as high as 10–18%, as in the case of ancient uraninites, then the interactions between the different isotopes (in determining the complex spectrum of vibrational frequencies) cannot be neglected. Here the difference between the diffusion constants will be even less than that indicated above. In general, we can neglect the effect of isotopic mass in discussing diffusion in radioactive minerals.

Effect of Various Factors on the Diffusion Coefficient

There are three factors which could bring about an appreciable change in the value of the diffusion coefficient, D, which has been assumed constant throughout the history of the crystal:

(1) The effect of the increasing concentration of the daughter product: In the case of uraninites, where concentrations of 18% Pb are recorded, this effect would deserve consideration. Where the Pb concentration is small ($<0{\cdot}1$%, as in zircon), the slow increase in the Pb concentration will only exert a small effect on the diffusion coefficient—see Jost (1952, p. 240–245).

(2) The effect of radiation damage: The response of radioactive minerals to the continued bombardment of the structure by alpha particles and recoil nuclei varies greatly. The largest changes in the value of the diffusion constant are to be expected in the case of minerals which enter the metamict state, the nature of which was reviewed by Pabst (1953). The metamictization of zircon has been studied in detail by Holland and Gottfried (1955), who distinguish between three stages in the process. Initially, there is a general distension of the structure, brought about by a homogeneous distribution of direct "knock-on" displacements of the lattice. Optical and X-ray data showed that a second phase consists of small crystallites which are not aligned with the residual structure from the first stage, and a third phase is apparently identical with $ZrSiO_4$ glass.

These results have a twofold importance in considering solid diffusion in zircon. Firstly, the additional vacancies and interstitial ions present in damaged zircon might be expected to raise the diffusion coefficient (see Glen, 1955, p. 427), and secondly, the formation of disoriented crystallites presents the possibility of grain-boundary diffusion taking place along the crystallite boundaries. The process of grain-boundary diffusion has recently been reviewed by Smoluchowski (1952, p. 464) and Le Clair (1953, p. 280). Both theory and experiment show that (for a particular structure) the grain-boundary diffusion constant is raised and the activation energy lowered, compared to the values of these parameters for diffusion in the lattice alone. In the case of Ag metal, the values of the activation energy for lattice and grain-boundary diffusion are 46 kcal/mole and 21 kcal/mole, respectively. (In this case the average grain-size of the polycrystalline material was 35 μ, and the width of the boundary estimated at 5 Å.)

(3) The effect of past changes in temperature: For two different absolute temperatures, T_1 and T_2, we have the relation

$$D_{T_2} = D_{T_1} \exp \{ Q/R \, (1/T_1 - 1/T_2 \} \qquad (6)$$

where Q = activation energy for diffusion of the daughter element in the radioactive mineral,

R = gas constant.

We have effectively assumed a constant temperature during the entire history of the crystals. The validity of this naïve assumption can only be tested by examination of the stratigraphy in each individual region. For example, in the case of the Cape granite, South Africa, which was probably formed ~600 million years ago, this region suffered extensive uplift and peneplanation, becoming exposed to the surface and receiving sediments, including glacial debris, 300 million years ago (deposition of the Cape System, approximately 3 km thick). Since the formation of the granite the region has not suffered any folding or regional metamorphism. Erosional processes brought the region very close to the surface by mid-Tertiary time. There is no evidence of igneous activity in the region since the formation of the granite, save for the occurrence of a few thin and widely scattered basaltic dykes. There is some evidence, therefore, that the temperature of this granite at Cape Town may have been close to surface temperature for a considerable portion of the past 600 million years.

If we adopt the assumption that the temperature of this region has not deviated far from 300°K, there is a reasonable procedure for estimating whether the calculated Pb diffusion coefficient of $\sim 5 \times 10^{-23}$ cm^2/sec (see Table 4) is a plausible value: Through the use of equation (6), published experimental data on the diffusion coefficients of impurity cations in silicates may be reduced to room temperature values, which may be then compared with the above-mentioned figure.

The experimental data of Rosenqvist (1949, p. 569), reduced to 300°K, are given in Table 5.

Table 5.

Host mineral and direction of diffusion	Diffusing cation	Diffusion coefficient
Microperthite, $\perp\{001\}$	Pb^{2+}	1×10^{-21}
Albite, $\perp\{001\}$	Pb^{2+}	$1{\cdot}3 \times 10^{-31}$
Microperthite, $\perp\{001\}$	Ra^{2+}	$1{\cdot}3 \times 10^{-21}$
Microperthite, $\perp\{010\}$	Ra^{2+}	$1{\cdot}0 \times 10^{-21}$
Microperthite, $\neq[100]$	Ra^{2+}	$1{\cdot}4 \times 10^{-23}$
Albite, $\perp\{001\}$	Ra^{2+}	$1{\cdot}6 \times 10^{-25}$
Albite, $\perp\{010\}$	Ra^{2+}	4×10^{-25}
Albite, $\neq[100]$	Ra^{2+}	2.1×10^{-25}

Seven of the eight experiments conducted by Rosenqvist yield room-temperature (extrapolated) values of the diffusion coefficient lying between 10^{-21} cm^2/sec and 10^{-25} cm^2/sec; we may therefore conclude that, to a first approximation, the calculated value of 5×10^{-23} cm^2/sec for Pb diffusion in the Cape zircon is not an implausible value. Rosenqvist (1949a) has also studied the theory of lead diffusion in uranium minerals, though under much more restrictive assumptions than those which have guided the present work. However, it is of interest to note that Rosenqvist calculated values of D of the same order of magnitude as those obtained here.

There are no reliable data available which could enable us to estimate the value of the activation energy (Q) for diffusion of Pb in zircon. It should be stressed, however, that a particular range of values for both the diffusion coefficient and the activation energy of Pb diffusion in zircon must exist, and in principle these parameters are capable of measurement.

At this stage we may profitably state some of the important assumptions governing age measurements on granitic rocks through U-Th-Pb analyses on their zircons:

(i) The growth of most of the zircon crystals took place during an interval which was short compared to the age of the rock, that is, at a "date" which we denote t_0.

(ii) *Either*, at the date t_0 there were no remnant zircon crystals which survived from the pre-existing rock mass, *or*, the environment at the date t_0 was of such a nature that all lead was expelled from remnant zircon crystals surviving from the pre-existing rock mass. For example, the ruling temperature at the date t_0 may have been sufficiently high for all the lead to have been expelled from these crystals by solid diffusion.

Zircon crystals containing cores of rounded zircon—apparent survivors from an older generation—are not uncommon in certain granitic rocks; an estimate of the value of the Pb diffusion coefficient at magmatic or near-magmatic temperatures would assist in evaluating the U-Th-Pb age measurements which have been made on such materials.

A Crucial Test of the Magnitude of Daughter Isotope Diffusion in Radioactive Minerals

It is possible to design an experiment which can uniquely determine the feasibility of daughter-isotope diffusion in a radioactive mineral. This possibility arises from the presence of the term in "a^2" in equation (3). For a particular locality, age analyses should be performed on several mineral samples, possessing a hundredfold variation in grain size. The smallest-sized crystals should have effective spherical radii of a few hundredths of a millimetre. Our diffusion theory predicts that (i) an increasingly discrepant age pattern will be found with a diminution in grain size, (ii) a plot of "true age" vs. the parameter D/a^2, as in Fig. 6, will show an intersection at only one value of the true age for each of the several mineral samples; furthermore, the values of D/a^2 for these intersections should vary in inverse proportion to the *measured* values of a^2 pertaining to each sample.

A further test of the validity of daughter-isotope diffusion can be made by comparison, of the "true age" yielded by this theory, with age results on coexisting minerals, using completely independent decay schemes.

Conclusion

The process of daughter-isotope diffusion is proposed as a *possible* cause of the discrepant age measurements obtained from the use of several decay schemes. This mechanism deserves consideration because it can be tested in a quantitative manner, a merit not possessed by certain other theories in the field of geologic time studies.

Acknowledgements—The author is indebted to Dr. A. L. Hales and Dr. N. D. Clarence of the Bernard Price Institute for discussions concerning diffusion in minerals. Mr. C. W. Cryer of the National Physical Laboratory assisted the author with the mathematical aspects of this work, and Mrs. J. Harris carried out the bulk of the arithmetic computations.

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Appendix 1.

Setting $f = C + N_0 e^{-\lambda t}$, the equation becomes

$$\partial f/\partial t = D\nabla^2 f$$

and the initial and boundary conditions

$$f = C_0 + N_0 \qquad t = 0$$
$$f = N_0 e^{-\lambda t} \qquad \text{all } t,\ r \geqslant a.$$

A solution for this equation is given by Carslaw and Jaeger (1950, p. 200). Adopting the substitution $d^2 = \lambda a^2/D$

$$f = \frac{2}{ar} \sum_{n=1}^{\infty} \exp\left(-\lambda t n^2\pi^2/d^2\right) \sin n\pi r/a$$
$$\cdot \left[\int_0^a r'\psi(r') \sin\left(n\pi r'/a\right) dr' - n\pi D(-1)^n \int_0^t \exp\left(\lambda n^2\pi^2 r'/d^2\right)\phi(r')\, dr' \right]$$

where $\psi(r') = C_0 + N_0$ and $\phi(r') = N_0 e^{-\lambda r'}$.

After evaluating the integrals we obtain

$$f = \frac{2}{ar} \sum_{n=1}^{\infty} (-1)^n \sin\left(n\pi r/a\right)$$
$$\cdot \left\{ \exp\left(-\lambda t n^2\pi^2/d^2\right) \left[-\left(\frac{a}{n\pi}\right)^2 n\pi \overline{C_0 + N_0} + \frac{n\pi D N_0}{\lambda(n^2\pi^2/d^2 - 1)} \right] - \frac{e^{-\lambda t} n\pi D N_0}{\lambda(n^2\pi^2/d^2 - 1)} \right\}.$$

Now, because $C = f - N$, then $\bar{C}$, the average concentration over the whole sphere, is given by

$$\bar{C} = -N + 3/4\pi a^3 \int_0^a 4\pi r^2 \cdot f(r) \cdot dr$$
$$= -N + \frac{6N}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2 - d^2/\pi^2} + \frac{6}{a^2} \sum_{n=1}^{\infty} \exp\left(-\lambda t n^2\pi^2/d^2\right) \left[\frac{a^2}{n^2\pi^2} \overline{C_0 + N_0} - \frac{D N_0}{\lambda(n^2\pi^2/d^2 - 1)} \right].$$

Using the relation

$$\sum_{n=1}^{\infty} \frac{1}{x^2 - n^2} = \frac{\pi x \cot \pi x - 1}{2x^2}$$

given by Knopp (1948, p. 205) we have

$$\sum_{n=1}^{\infty} \frac{1}{n^2 - d^2/\pi^2} = \frac{\pi^2}{2d^2} \left[1 - d \cot d \right]$$

Making use of this substitution, and further algebraic identities, we obtain

$$\frac{\bar{C}}{N} = -1 + 3/d^2 - 3 \cot d/d + \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left\{\lambda t(1 - n^2\pi^2/d^2)\right\}}{n^2(1 - n^2\pi^2/d^2)}$$
$$+ \frac{6C_0}{N\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left\{-\lambda t(n^2\pi^2/d^2)\right\}}{n^2}$$

The last term is identical with the expression given by Jost (1952, pp. 45–46), for the diffusion

of a particular component out of a sphere, where there is no generation of this component by radioactivity,

i.e.
$$\frac{\bar{C}}{C_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2\pi^2 Dt/a^2)}{n^2}$$

Where the *initial* concentration of the daughter isotope is negligible, this term falls away, and the solution is found in the first four terms given above. The solution was given (without proof) by Wasserburg (1954).

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Argon und Helium als Kernreaktionsprodukte in Meteoriten

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(*Received* 23 *July* 1956)

Abstract—The investigations of Paneth, Reasbeck and Mayne have shown that iron meteorites contain a substantial proportion of He^3. The production of He^3 can be understood as an evaporation process, initiated by nuclear interactions of cosmic-ray particles. In this process the loss of some particles in an iron nucleus results in a nucleus with lower atomic weight. Small amounts of A^{36} and A^{38} have been found with a sensitive mass spectrometer. The isotopic ratio of A^{38}/A^{36} is about 1·7 and to 100 He^3-atoms belong 6·6 A^{38}-atoms. Both results may be understood by the evaporation theory. A way is discussed to determine with aid of the radioactive residual nuclei Cl^{36} and K^{40} the intensity of cosmic radiation in former times (10^5 and 10^9 years respectively). A way in determining the age of iron meteorites by measuring the amount of disintegrated residual nuclei is pointed out.

Einleitung

In den letzten Jahren haben Paneth, Reasbeck und Mayne (1953) zeigen können, dass in dem Meteorhelium ein beträchtlicher Anteil an He^3 enthalten ist. Damit war die Vermutung von H.E. Huntley und C. A. Bauer bestätigt, dass ausserhalb der Erdatmosphäre die Intensität der kosmischen Strahlung gross genug sein kann, um in Meteoriten He zu erzeugen, dessen Menge mit der gefundenen vergleichbar ist. Das gefundene He ist als Verdampfungsteilchen bei Sternprozessen zu verstehen, die durch energiereiche Teilchen der primären und sekundären Komponente der Ultrastrahlung ausgelöst werden.

Nach der Kernverdampfungstheorie ist zu erwarten, dass nach der Emission von leichten Teilchen wie n, p, d, He^4, t, He^3, Restkerne mit kleinerem Atomgewicht als Eisen (=56) übrig bleiben. Es schien aussichtsreich, in Meteoriten solche abgebaute Kerne in Form von Argon zu suchen, da die Behandlung der Edelgase bezüglich Aufschluss und Reinigung relativ einfach ist. Zum Austreiben der Gase wurden die Proben in einem Hochfrequenzofen geschmolzen. Die Reinigung der Gase erfolgte durch chemisches Abbinden der unedlen Bestandteile. Mit einem empfindlichen Massenspektrometer (Smits und Zähringer, 1955) wurden sowohl die Isotopenzusammensetzung als auch die Mengen dieser Edelgase bestimmt. Der Nachweis solch kleiner Gasmengen ist durch das Auftreten von Störlinien erschwert, die einmal selbst im Massenspektrometer vorhanden sind und ausserdem beim Schmelzen im Graphittiegel erzeugt werden.

Messtechnik

1. *Aufschlussmethode*

Zum Austreiben der Gase wurden die Meteoritenproben durch induktives Erhitzen im Vakuum geschmolzen. In Abb. 1 ist der Schmelzofen schematisch dargestellt. In einem einseitig geschlossenen Quarzkolben sind Schmelztiegel, Probe und ein Eisentiegel untergebracht. Der Schmelztiegel ist aus Graphit und wird mit einem Hochfrequenzgenerator induktiv erhitzt. Die Leistung des Generators beträgt 6 KW und die erreichbare Tiegeltemperatur 1700°. Die Probe hängt zunächst noch über dem Schmelztiegel, um diesen vor dem

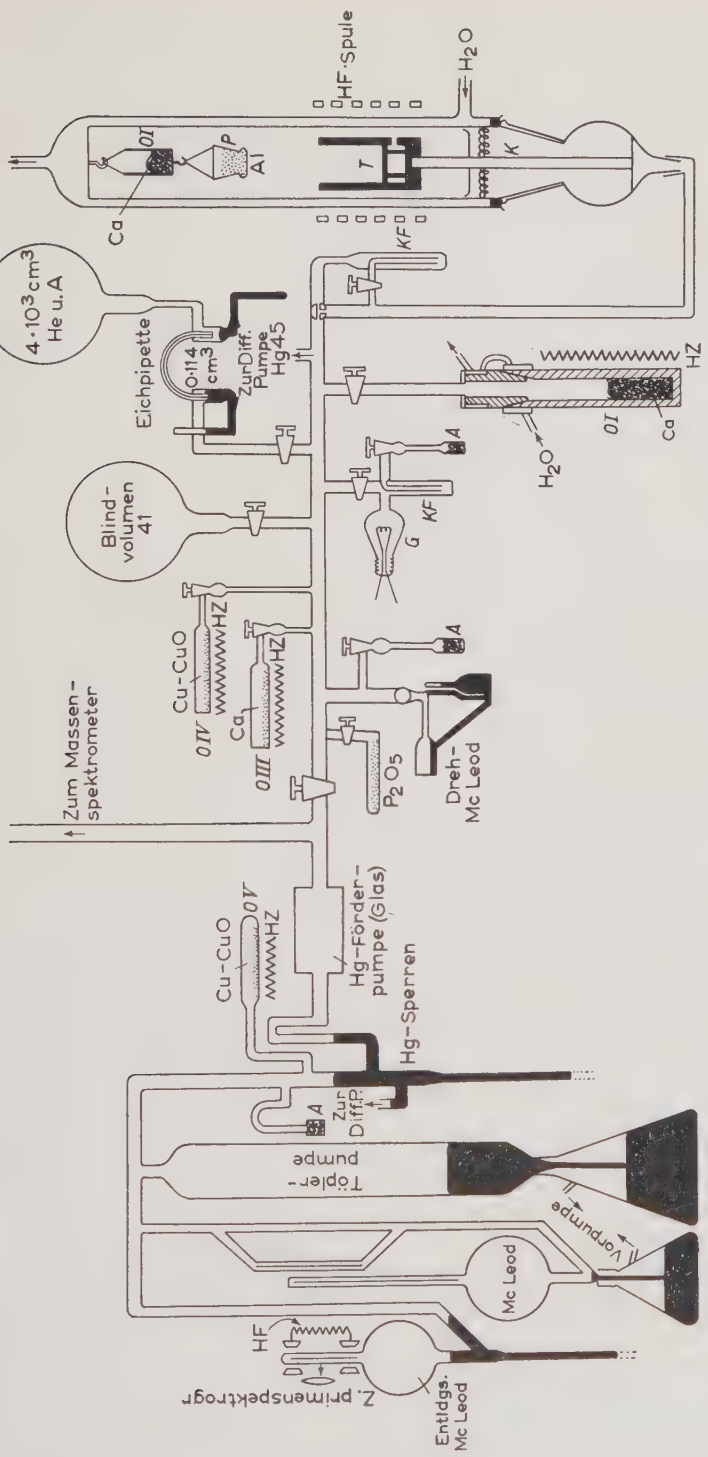

Abb. 1. *Aufschluss und Reinigungsapparatur P* Probe, *T* Graphittiegel, *Al* Durchschmelzfolie, *K* Keramikstab, *OI* Ca-Ofen mit *HF* geheizt, *OII* Ca-Ofen (V2A), *KF* Kühlfalle, *A* Aktivkohle, *G* Glühlampe (Crack-Ofen), *OIII* Ca-Ofen, *OIV*, *OV* Cu-CuO-Ofen, *HZ* Heizwicklung.

Schmelzen durch Erhitzen gut entgasen zu können. Meteoritenproben in Form von Spänen befinden sich in einem Glastrichter, der unten mit einer Aluminium folie zugebunden ist. Ganze Stücke werden an einer Drahtschleife aufgehängt. Um die Probe in den Tiegel fallen zu lassen, wird die Folie oder die Drahtschleife induktiv durchschmolzen. Zum völligen Austreiben der Gase aus dem Meteoreisen genügt es, die Probe etwa 10 Min. flüssig zu halten.

Die entwichenen Gase wurden nach früher schon beschriebenen Methoden [Gentner, Goebel und Präg (1955)] gereinigt und nur die Edelgasanteile abgetrennt. Ein solcher Reinigungsofen stellt der mit Calziumspänen gefüllte Eisentiegel dar, der ebenfalls induktiv erhitzt wird und das Eindringen von Atmosphärenluft durch heisse Ofenwände verhindert.

2. *Edelgasbestimmung*

Nach der groben Reinigung mit dem Calziumofen wird das Helium vom Argon mit gekühlter Aktivkohle getrennt und beide Komponenten nachgereinigt. Beim Helium sind besonders Verunreinigungen an Wasserstoff zu beseitigen, da sonst die He^3/He^4-Analyse durch die Verbindung HD^+ und H^{3+} gestört wird. Mit einem Cu-CuO-Ofen wird der Wasserstoff bei ca. 300°C zu Wasser verbrannt.

Da es sich beim Argon um äusserst kleine Gasmengen handelt, waren besondere Kontrollversuche erforderlich, um mit Sicherheit Störlinien von Kohlenwasserstoffen mit den Massen 36 und 38 auszuschliessen:

(a) Mit Aktivkohle wurde bei −70°C das Argon in zwei Teile getrennt und einzeln im Massenspektrometer untersucht. Bei Anwesenheit von Kohlenwasserstoffen müsste die an der Aktivkohle absorbierte Komponente eine verschiedene Isotopenzusammensetzung aufweisen.

(b) Mit einer geschmolzenen Probe wurde ein Leerversuch durchgeführt, sodass zur Bildung von Kohlenwasserstoffen im Graphittiegel dieselben Bedingungen vorlagen. Das gefundene Argon hatte die Isotopenzusammensetzung von Luftargon.

(c) Schliesslich wurde das gefundene Gas einer heissen Wolframwendel (Glühlampe) ausgesetzt, an der die Kohlenwasserstoffe in Bruchstücke mit kleineren Massenzahlen als 36 gekrackt werden. Auch dieser Prozess hatte auf das Ergebnis keinen Einfluss und es kann mit Sicherheit angenommen werden, dass die auf den Massenzahlen 36 und 38 gefundenen Gase nur Argonisotope sind.

3. *Massenspektrometrische Analyse*

Der Aufbau des Spektrometers ist bereits von Smits und Zähringer (1955) beschrieben. Es handelt sich um ein magnetisches 60°-Spektrometer mit Elektronenstossionenquelle und elektrischem Nachweis der Massenhäufigkeit.

Zur Durchführung der vorliegenden Arbeit musste die Nachweisempfindlichkeit noch weiter gesteigert werden. Diese ist bestimmt durch die Ausbeute der Ionenquelle (Verhältnis der am Auffänger ankommenden zu eingelassenen Gasatomen) und durch die Intensität der Störlinien auf der betr. Massenzahl. Die von Smits und Zähringer (1955) beschriebene Ionenquellenanordnung ermöglicht theoretisch eine Ausbeute von 1%, wovon etwa 10% erreicht wurden. Zur Beseitigung der Störlinien befindet sich in der Ionenquelle selbst eine Kühlfalle, die mit flüssiger Luft gekühlt wird. Durch Ausheizen der Ionenquelle und gründliches Abpumpen können die Störlinien auf den Massenzahlen 36 und 38 kleiner gehalten werden als z.B. 10^{-8} cm^3 Argon 38 entsprechen. Zur Beseitigung der HD-Störlinie wurde an die Ionenquelle ein mit flüssiger Luft gekühltes Aktivkohlerohr angeschlossen, das ohne das Helium messbar zu adsorbieren als selektive Pumpe wirkt. Das Gas wurde nicht über einen gefetteten Hahn, sondern mit Hilfe einer Quecksilbersperre oder eines magnetischen Kugelventils in die Ionenquelle eingelassen. Zur Kontrolle der HD-Linie wurde während der Messung die H_2-Intensität überprüft. So können ohne Berücksichtigung eines Störuntergrundes 10^{-7} cm^3 He^3 nachgewiesen werden.

Die quantitative Bestimmung der kleinen Gasmengen wurde nicht nach dem sonst üblichen Isotopenverdünnungsverfahren durchgeführt; die Konstruktion der Ionenquelle ermöglicht eine einfachere Methode zur Mengenmessung. Die gesamte Gasmenge wird in kurzer Zeit in den Ionenquellenraum hineingepumpt. Zwischen Ionenquellenraum und Ionenrohr befindet sich zur

Drosselung des Gasverbrauchs ein Bremskanal. Der Druck und damit die Linienintensität steigen so schnell auf ein Maximum an, um dann exponentiell abzufallen. Die maximale Linienintensität ist der eingelassenen Gasmenge proportional. Die Eichung des Massenspektrometers erfolgt vor und nach der Messung mit einer kalibrierten Gasmenge, die unter denselben Versuchsbedingungen und auf demselben Wege in die Ionenquelle eingelassen wird. Während des zeitlichen Druckabfalles werden über einen Doppelauffänger gleichzeitig 2 Linien automatisch registriert. Die Isotopenzusammensetzung wird auf den Anfangswert extrapoliert, wo noch keine Entmischung durch den Bremskanal stattgefunden hat.

Messergebnisse

In Tabelle 1 sind die gefundenen Helium- und Argonwerte und Isotopenzusammensetzungen von 8 verschiedenen Meteoriten eingetragen. Mit zunehmendem Heliumgehalt macht sich gegenüber Luftargon eine deutliche Isotopen-

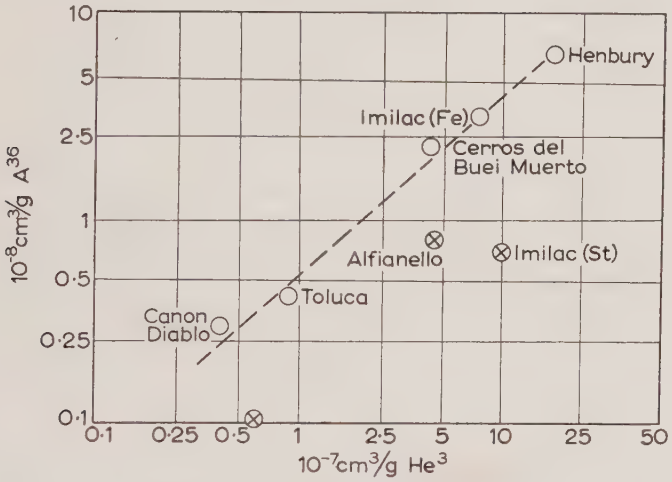

Abb. 2. A^{36} und He^3-Gehalt von 8 verschiedenen Meteoritenproben (○ Eisenmeteorite, ⊗ Steinmeteorite).

verschiebung zu Gunsten A^{36} und A^{38} bemerkbar. Dieses Ergebnis lässt vermuten, dass eine dem Helium proportionale Menge Argon mit ganz anderem Häufigkeitsverhältnis als Luftargon in den Meteoriten vorhanden ist und mit einer gewissen Menge Luftargon, die beim Aufschliessen und Reinigen unvermeidbar in die Apparatur eindringt, vermengt ist. Zur Korrektur dieses Luftargons wurde angenommen, dass A^{40} und A^{36} etwa gleich häufig gebildet wurde, d.h. dass das gefundene A^{40} praktisch alles aus der Luft stammt (vergl. spätere Diskussion). Entsprechend der Isotopenzusammensetzung von Luftargon wurde die Korrektur auf $A^{40} = 1$ vorgenommen und in Tabelle 1, Spalte 6 das so gewonnene Verhältnis von A^{38} zu A^{36} eingetragen. Im Mittel ist dies für alle Meteoriten etwa 1,7.

In Abb. 2 ist die korrigierte Menge A^{36} gegen den He^3-Gehalt aufgetragen. Die fünf Messpunkte der Eisenmeteorite liegen über ca. 2 Grössenordnungen auf einer "Geraden" und auf 100 He^3-Atome werden etwa 10 A^{36}- $+A^{38}$-Atome gefunden. Die Messpunkte der Steinmeteorite liegen deutlich unterhalb der "Geraden."

Die ungefähre Proportionalität von He^3 und A^{36}, A^{38} lässt auf den selben Entstehungsprozess schliessen. Die Abweichungen bei den Steinmeteoriten lassen

Tab. 1. Meßergebnisse von 5 Eisen- und 3 Steinmeteoriten

Name des Meteoriten	(a) $He^3 + He^4$ 10^{-6} cm^3/g	(b) He^3/He^4	(c) He^3 in 10^{-7} cm^3/g	(d) Gefundenes Isotopenverhältnis $A^{36} : A^{38} : A^{40}$	(e) Auf $A^{40} = 1$ korrig. Verhältnis $A^{36} : A^{38}$	(f) A^{36} 10^{-8} cm^3/g	
Henbury	9,6	0,22	17,3	1 : 1,37 : 58	1 : 1,66	6,9	
Imilac (Eisenphase)	3,7	0,25	7,4	1 : 0,90 : 156	1 : 1,70	3,1	
Cerros del Buei Muerto	3,1	0,16	4,3	1 : 0,95 : 148	1 : 1,7	2,2	Eisenmeteorite
Toluca	0,5	0,21	0,9	1 : 0,50 : 234	1 : 1,6	0,4	
Canon Diablo	0,4	0,11	0,4	1 : 0,42 : 256	1 : 1,8	0,3	
Imilac (Steinphase)	7,9	0,15	10	1 : 0,35 : 270	~1 : 2	~0,7	
Alfianello	4,5	0.12	4,8	1 : 0,62 : 220	1 : 1,8	0,8	
Holbrook*	3,2	0,02	0,6	1 : 0,70 : 197	1 : 1,7	0,1	Steinmeteorite
Isotopenzusammensetzung von Luftargon				1 : 0,187 : 296			

* Einwaage nicht genau bekannt

vermuten, dass die Argonerzeugung mit dem Eisengehalt verknüpft ist. Während die He^3- und He^4-Atome als Verdampfungsteilchen entsprechend den schweren Spuren in Photoplattensternen gedeutet werden, wird man das Argon eher als Restkerne verstehen, die nach dem Abdampfen solcher Teilchen von den Eisenkernen übrig geblieben sind. Man müsste sonst Neon mindestens ebenso häufig finden. Das Experiment ergab jedoch bei dem Meteoriten "Henbury" für Ne^{20} einen Wert, der etwa 5 mal kleiner ist als der von A^{38}.

Das überschüssige He^3 bei den Steinmeteoriten kann beim Verdampfen der übrigen Kerne (O_2, Si, Mg) entstanden sein, deren Atomgewicht kleiner als Argon ist und deren Restkerne somit keinen Beitrag zu Argon liefern können.

Die oben beschriebene Korrektur setzt voraus, dass kein A^{40} durch den K-Zerfall von K^{40} vorhanden ist. Dies ist erfüllt, wenn bei einem angenommenen Meteoritenalter von 10^9 Jahren der Kaliumgehalt kleiner als 10^{-4} g K/g Meteoreisen beträgt. Für Eisenmeteorite liegen in der Literatur keine Kalium-Analysen vor. Der Kaliumgehalt ist jedoch sicher kleiner als in Steinmeteoriten, in denen sich nach (Ahrens, Pinson und Kearns, 1952) einige 10^{-4} g K/g Substanz befinden. Eine Verfälschung durch radiogenes Argon ist bei den Eisenmeteoriten also nicht zu befürchten, während bei den Steinmeteoriten das A^{38}-/A^{36}-Verhältnis etwas zu gross sein kann.

Die Fragen, ob Argon schon primär in den Meteoriten gelöst war, und ob Argonkerne der Ultrastrahlung im Eisen stecken blieben, können durch die Abschätzung des Neons verneint werden.

Disskussion der Ergebnisse

(a) Theorie:

Bei Reaktionen energiereicher Teilchen wird der Massenverlust von Kernen überwiegend durch Verdampfen von langsamen leichten Teilchen verursacht (Sternprozess). Dieser Vorgang ist in Übereinstimmung mit der Erfahrung einigermassen aufgeklärt. Der Nachweis solcher Restkerne in Photoplatten ist allerdings nicht möglich, da ihr Impuls zu klein ist.

Nach der Kernverdampfungstheorie wächst die Zahl der verdampften Nukleonen mit der Anregungsenergie und während des Verdampfungsprozesses sollen sich die Restkerne nicht allzu weit von der Sohle des Energietals entfernen. Zunächst werden zwar etwas mehr Neutronen emittiert. Wenn die gesamte Anregungsenergie jedoch kleiner wird als 10 MeV, hört die Neutronenemission auf, während Protonen, deren entsprechende Niveaus im Potentialtopf höher liegen, noch durch die Potentialschwelle hindurchgelangen können. Das Neutronendefizit wird wieder ausgeglichen, und der Restkern gelangt in den stabilen Bereich des Energietals. Die restliche Anregungsenergie wird durch γ-Strahlung abgegeben und die instabilen Kerne werden entsprechend der Lage im NZ-Diagramm durch β-Übergänge stabile Plätze aufsuchen. Dadurch werden die Kerne nur längs einer Isobaren verschoben, d.h. die Summe der Restkerne ist zunächst festgelegt und wird sich entsprechend der Zahl der stabilen isobaren Kerne verteilen.

(b) Wie die Verhältnisse speziell für Argon liegen, wird in Abb. 3 gezeigt. Die Isobare 38 ist nur durch A^{38} vertreten, während es 3 isobare Kerne mit der

Masse 36 gibt, wovon Cl^{36} mit einer Halbwertszeit von $4{,}5 \cdot 10^5$ Jahren durch β^--Zerfall in A^{36} übergeht. Bei einem minimalen Meteoritenalter von 10^8 Jahren kann man für die folgenden Betrachtungen annehmen, dass praktisch alles Cl^{36} zerfallen ist. Man erwartet also, dass A^{38} als einziger stabiler Kern auf der Isobaren 38 am häufigsten ist, während etwa dieselbe Anzahl Restkerne auf S^{36} und A^{36} verteilt wird. Nimmt man an, dass die Summen der Restkerne auf der Isobaren 36 und 38 etwa gleich gross sind, was bei benachbarten Isobaren näherungsweise zutreffen wird, und dass die drei isobaren Kerne A^{36}, Cl^{36} und S^{36} gleichhäufig gebildet wurden, dann muss sich nach dem Zerfall des Cl^{36} in A^{36} für

$$\frac{A^{36} + S^{36}}{A^{36}} = \frac{A^{38}}{A^{36}} = 3/2 \text{ ergeben.}$$

In diesem Fall würde der Streifen symmetrisch in der Talsohle liegen und wäre nur 3 Masseneinheiten breit. Der experimentell gefundene Wert für A^{38}/A^{36} ist mit 1,7 etwas grösser. Eine bessere Übereinstimmung kann bei den obigen Annahmen jedoch nicht erwartet werden. Die Verteilung der Restkerne auf einer Isobaren wird nicht gleichmässig sein, sondern mit der Entfernung von der Talsohle entsprechend der geringeren Stabilität abnehmen. So müsste z.B. Cl^{36} etwas häufiger gebildet werden als A^{36}. Auch hinsichtlich der Symmetrie eines Kernes (N, Z = gerade oder ungerade) können die Erzeugungsquerschnitte Schwankungen aufweisen. Ferner werden entgegen der obigen Annahme die Restkerne auf den isobaren 36 und 38 nicht gleich häufig entstehen, da eine Abnahme der Häufigkeit mit zunehmender Zahl der verdampften Nukleonen zu erwarten ist.

Das gefundene Verhältnis für A^{38}/A^{36} kann schliesslich auch direkt mit den Ergebnissen von Laboratoriumsversuchen verglichen werden.

Batzel u.a. (1952) haben Kupfer mit Protonen (340 MeV) bestrahlt und durch Aktivitätsmessung die Erzeugungsquerschnitte einiger radioaktiver Restkerne gemessen und durch Interpolation die Werte für benachbarte Kerne abgeschätzt. Die Energie der Protonen von 340 MeV entspricht zwar nicht der Energie der sternerzeugenden Strahlung in einem Meteoriten. Nun ist aber der Verdampfungsprozess und damit auch die Entstehung der Restkerne weitgehend von der Art der Anregung unabhängig, sodass die relative Häufigkeit der einzelnen isobaren Restkerne immer dieselbe sein wird. In der folgenden Tabelle sind die von Batzel gemessenen und abgeschätzten relativen Erzeugungsquerschnitte für die Isobaren 36 und 38 (bezogen auf $Cu^{61} = 1$) zusammengestellt:

S^{36}	0,003		K^{38}	0,0025	
Cl^{36}	0,005	$= 0{,}008$	A^{38}	0,01	0,015
A^{36}	0,003		Cl^{38}	0,0025	

Dem im Meteoriten gefundenen Verhältnis A^{38}/A^{36} entspricht das Verhältnis der Erzeugungsquerschnitte von

$$\frac{K^{38} + A^{38} + Cl^{38}}{A^{36} + Cl^{36}} = \frac{0{,}015}{0{,}008} = 1{,}8. \quad \text{(Vgl. Abb. 3)}$$

Die Übereinstimmung mit dem gefundenen Wert von 1,7 ist unter Berücksichtigung der ganz verschiedenen Messmethoden erstaunlich gut.

(c) Zur Deutung der gefundenen Argonmengen wird man diese zweckmässig auf He^3 beziehen, das als Maß für die Bestrahlung angesehen werden kann.

Auf 100 He^3-Atome kommen bei Eisenmeteoriten etwa 6,6 A^{38}-Atome. Das Atomgewicht von Eisen beträgt 56. Zur Entstehung von einem A^{38}-Atom müssen also 18 Nukleonen verdampfen. Dies entspricht einer Anregungstemperatur

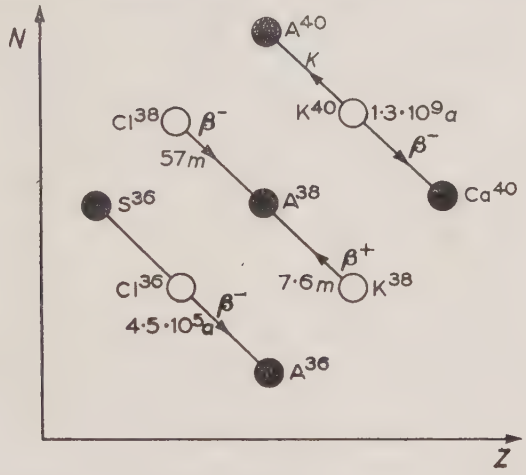

Abb. 3. N,Z-Diagramm der Isobaren 36, 38 u. 40.

von 6 MeV (Energie pro Nukleon) bzw. einer mittleren Kerntemperatur von 2,4 MeV (vgl. Hagedorn und Macke, 1953). Aus den spezifischen Emissionsverhältnissen kann man entnehmen, dass bei einem solchen Verdampfungsprozess etwa 0,6 (He^3 + H^3)-Teilchen beteiligt sind. Unter Berücksichtigung des Zerfalls von H^3 (β^--Strahler mit 12 Jahren Halbwertszeit) in He^3 müssen bei der Bildung von 6,6 A^{38}-Atomen also rund 4 He^3-Teilchen frei werden, sodass die gefundenen 100 He^3-Atome zur Entstehung der Restkerne weiterer 25 Isobaren ausreichen, wenn Argon als Maß für deren mittleren Häufigkeit angesehen wird. Ausserdem ist zu beachten, dass bei der Entstehung der Restkerne der ersten 10 Isobaren unterhalb des Atomgewichts 56, d.h. bei kleinen Kerntemperaturen ($<1,5$ MeV) praktisch kein He^3 und H^3 emittiert wird und somit betrifft die obige Abschätzung nur die Restkerne mit den Atomgewichten <46. Für die Häufikeit dieser noch verbleibenden Restkerne ist deshalb A^{38} ein vernünftiger Mittelwert (vergl. Abb. 4).

Um sich über den Verlauf der Restkernverteilung ein qualitatives Bild zu verschaffen, ist man vorläufig auf die Ergebnisse der Untersuchungen an Photoplattensternen angewiesen. Aus Sterngrössendiagrammen ist zu entnehmen, dass die Häufigkeit der Ereignisse mit der Zahl der Verdampfungsspuren etwa exponentiell abnimmt.

Einen entsprechenden Verlauf kann man auch für die Verteilung der Restkerne erwarten. Diese Vermutung wird durch die Abschätzung des Neongehaltes bestätigt: Der Entstehung von Argon und Neon als Restkern aus Eisen entsprechen

Sterne in Photoplatten mit 7 bzw. 12 "schweren" Spuren und deren Häufigkeit wird in Photoplatten im Verhältnis 4 : 1 gefunden, während das Verhältnis A^{38} zu Ne^{20} in Eisenmeteoriten etwa 5 : 1 beträgt.

Der Neongehalt einiger Eisenmeteorite ist inzwischen von Reasbeck und Mayne veröffentlicht worden. In Abb. 4 ist die so vermutete Verteilungskurve angegeben. Die schraffierte Fläche soll die Abschätzung der Restkerne aus dem He^3-Gehalt in der Umgebung von A^{38} veranschaulichen.

Diese Verteilung wird allerdings von der Energie abhängen. Da die heliumarmen Proben wahrscheinlich aus tieferen Lagen eines Meteoriten stammen, war die Energie der sternauslösenden Teilchen in Mittel auch geringer. Das He^3: Ne: A-Verhältnis wird also nicht für alle Meteoritenproben dasselbe sein.

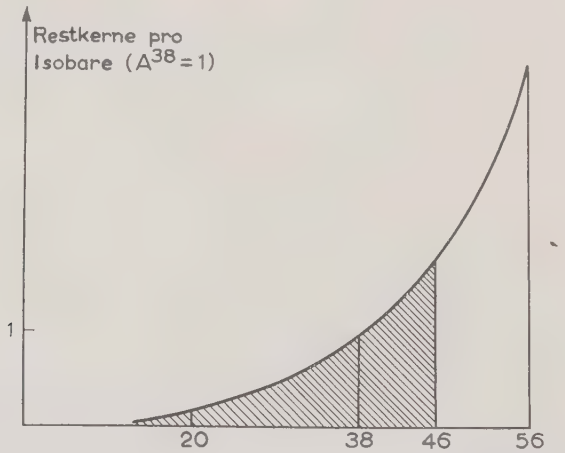

Abb. 4. Häufigkeitsverteilung der Restkerne wie nach Sterngrössendiagrammen zu erwarten ist.

(d) Im Zusammenhang mit den später noch zu diskutierenden Messungen von Fireman (1955) interessieren die Messwerte des Pallasiten Imilac. Dieser ist ein schwammartiges Gebilde aus Eisen, dessen Hohlräume mit Olivin gefüllt sind. Der Bau des Meteoriten garantiert also gleiche Bestrahlung beider Phasen. Diese wurden getrennt auf Helium und Argon untersucht. Die Heliumwerte sind in der folgenden Tabelle eingetragen:

	$He^4 \times 10^{-6}$ cm³/g	$He^3 \times 10^{-7}$ cm³/g
Eisenphase	3	7,4
Steinphase	6,9	10

Die Steinphase enthält etwa 35% mehr He^3 als die Eisenphase. Dieses Ergebnis lässt sich mit Messungen von Fireman (1955) und Fireman und Rowland (1955) vergleichen, die wie bei Eisen auch an leichteren Kernen (N_2, O_2) den Erzeugungsquerschnitt für Tritium gemessen haben. Sie finden für Stickstoff und Sauerstoff

28 ± 4 bzw. 33 ± 4 mb. (Eisen $= 67 \pm 7$ mb). Berechnet man nach diesen Erzeugungsquerschnitten für einen Steinmeteoriten entsprechend seiner mittleren Zussammensetzung von 35% O_2, 25% Fe, 18% Si, 14,5% Mg die Tritiumerzeugung pro g Material, so sollte diese 30% grösser sein als bei Eisen.

Die Messwerte des Meteoriten Imilac bestätigen also das relative Verhältnis der Tritiumerzeugungsquerschnitte bezüglich der verschiedenen Atomgewichte recht befriedigend.

Ausserdem lassen sich aus dem He^4-Gehalt Aussagen über Erzeugungsquerschnitte dieses Isotops machen. Der radiogene He^4-Anteil ist nach dem He^3/He^4-Verhältnis vermutlich klein. Die Steinphase enthält etwa doppelt so viel He^4 als die Eisenphase. Dieses Ergebnis stimmt qualitativ mit den Beobachtungen von Page (1950) überein, wonach das Verhältnis der doppelt geladenen Teilchen zur Gesamtzahl der Spuren bei leichten Kernen auch etwa doppelt so gross ist wie bei schweren. Dies bedeutet, dass in leichten Kernen bevorzugt He^4-Teilchen abgespaltet werden.

(e) Meteoriten als Integrator der Höhenstrahlung:

Während die Meteorite durch den Weltenraum flogen, wurden die Reaktionsprodukte seit Milionen von Jahren in bestimmter Weise aufgespeichert. Bei bekannter Intensität und Energieverteilung der kosmischen Strahlung zu früheren Zeiten könnte man aus der Menge der Reaktionsprodukte das Alter der Meteore abschätzen. Andererseits lässt sich aus den noch radioaktiven Produkten entsprechend ihrer Zerfallszeit etwas über die Intensität der kosmischen Strahlung ausserhalb der Erde und zu früheren Zeiten aussagen. Versuche in dieser Richtung haben Martin (1953), Fireman (1955), und Fireman und Schwarzer (mündliche Mitteilung) unternommen.

Martin findet für den Meteoriten Bethany eine Bestrahlungszeit von $2{,}5 \cdot 10^8$ Jahren, wenn mit der 1949 am Nordpol gemessenen Höhenstrahlungsintensität gerechnet wird. Das nach dem radiogenen Heliumgehalt bestimmte Alter ist um den Faktor 3 kleiner. Martin möchte hieraus den Schluss ziehen, dass die Intensität der Höhenstrahlung während dieser Zeit im Mittel 3-mal grösser war als heute. Zu einem entsprechenden Ergebnis führen die Versuche von Fireman (1955). Mit dem Protonen-Synchrotron in Brookhaven wurde bei 2,2 BeV der Erzeugungsquerschnitt von Tritium an Eisen gemessen. Tritium lässt sich mit dem in Meteoriten gefundenen He^3 vergleichen, da bei der Kernverdampfung viel mehr Tritium als He^3 emittiert wird und Tritium mit einer Halbwertszeit von 12 Jahren in He^3 zerfällt. Für den Erzeugungsquerschnitt von Tritium an Eisen ergaben sich 67 mb. Zur Bildung von 10^{-5} cm^3 He^3, wie es in dem Meteoriten Morden von Paneth und Mitarb. gefunden wird, wäre demnach eine Zeit von 7×10^9 Jahren erforderlich. Da man annehmen kann, dass Meteoriten mit noch höherem He^3-Gehalt existieren—schon deshalb, weil beim Flug durch die Atmosphäre die äussere Schicht der Meteoriten abgedampft wird siehe so übertrifft dieser Wert sicher das maximale Weltalter, das zu 5—6 Millarden Jahre angenommen wird. Man muss also aus diesem Ergebnis den Schluss ziehen, dass die mittlere Strahlungsintensität am Ort des Meteoriten grösser war, als sie heute bei uns in der Polargegend gemessen wird. Dies kann bedeuten, dass die Intensität der

kosmischen Strahlung zu früheren Zeiten grösser war oder dass weit ausserhalb der Erde eine intensivere Strahlung herrscht.

Fireman und Schwarzer haben ausserdem versucht, aus der Aktivität und dem oben angegebenen Erzeugungsquerschnitt von Tritium die Intensität der Höhenstrahlung zur Zeit des Meteoritenfalles zu bestimmen. Für den Meteoriten Norfork (gefallen 1918) finden sie 10 Teilchen/cm² sec, während 1949 die Intensität zu 3 Teilchen/cm² sec gemessen wurde. Hiernach würde man den hohen He^3-Gehalt an Meteoriten eher so deuten, indem man ausserhalb der Erde eine höhere Strahlungsintensität annimmt und eine zeitliche Änderung der Ultrastrahlung gar nicht zu sehr in Betracht zieht. Zu demselben Ergebnis führen auch Untersuchungen der C^{14}-Methode, wonach während der letzten 20.000 Jahre keine wesentliche Intensitätsänderung der Ultrastrahlung eingetreten sein kann.

Nach neuren Berichten Neher und Stern (1955) soll die primäre Komponente ausserhalb der Erde tatsächlich eine andere Energieverteilung besitzen, als man

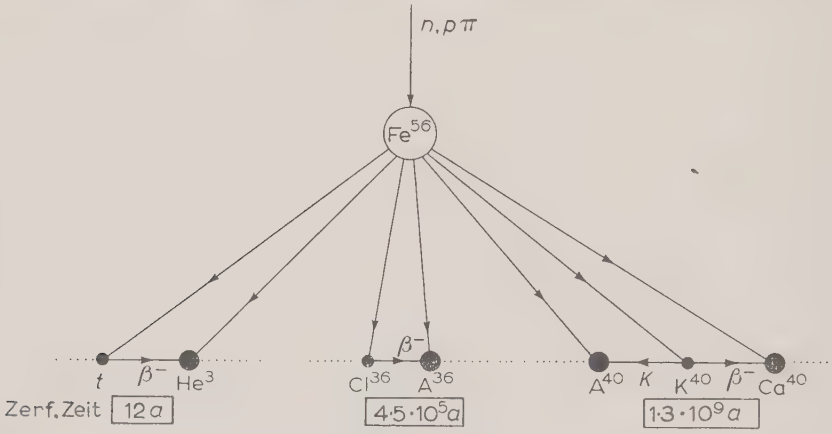

Abb. 5. Schematische Darstellung der Entstehung von radioaktiven Kernreaktionsprodukten aus Eisen.

bisher angenommen hat. Man beobachtet nämlich in nördlichen Breiten im Zusammenhang mit dem Sonnenzyklus beträchtliche Intensitätsschwankungen. Dies bedeutet, dass in der primären Strahlung auch energiearme Teilchen (<1 GeV) enthalten sind und der sogenannte "cut off" nicht existiert. Die Multiplizität bei diesen Energien ist zwar gering und verschwindet unterhalb 0,5 GeV (Wilson, 1952). Falls jedoch zusätzliche Teilchen mit 0,5—1 GeV zahlenmässig stark vertreten sind, wäre so der hohe He^3-Gehalt auch im Innern eines Meteoriten zu verstehen.

Während sich aus der Aktivität des Tritium etwas über die heutige Höhenstrahlungsintensität ausserhalb der Erdatmosphäre aussagen lässt, und der He^3-Gehalt einen mittleren Alterswert der Meteoriten ergibt, kann man aus den radioaktiven Restkernen Cl^{36} und K^{40} etwas über die Art der Bestrahlung zu früheren Zeiten erfahren. Cl^{36} ist β^--aktiv und zerfällt mit einer Halbwertszeit von $4{,}5 \cdot 10^5$ Jahren in A^{36}. Da das Alter der Meteore viel grösser ist als die Halbwertzeit, ist (wie bei Tritium) das durch die kosmische Strahlung erzeugte Cl^{36} mit der

zerfallenden Menge im Gleichgewicht. Die Aktivität von Cl^{36} ist also der Intensität der kosmischen Strahlung vor einigen 10^5 Jahren proportional. Durch Vergleichen der Tritium- und Cl^{36}-Aktivitäten könnte man daher etwas über die Intensitätsänderung der kosmischen Strahlung erfahren. Andererseits lässt sich bei bekanntem Verhältnis der Erzeugungsquerschnitte von Cl^{36} und A^{36} die zerfallene Menge Cl^{36} errechnen. Hieraus lässt sich eine weitere Methode zur Altersbestimmung entwickeln, die lediglich die Messung des A^{36}/Cl^{36}-Verhältnisses erfordert.

Entsprechende Überlegungen lassen sich für den Restkern K^{40} anstellen, der mit einer Halbwertszeit von $1{,}3 \cdot 10^9$ Jahren durch β^--Zerfall in Ca^{40} und durch K-Einfang in A^{40} übergeht. Da die Bestrahlungszeit vermutlich nicht sehr viel grösser war als die Halbswertszeit von K^{40}, hat sich das Gleichgewicht noch nicht eingestellt. Aus dem Verhältnis der erzeugten und zerfallenen K^{40}-Kerne kann man jedoch über die Bestrahlung vor etwa 10^9 Jahren Aufschluss erhalten.

Die experimentellen Schwierigkeiten dieser Untersuchungen werden die Messungen der sehr kleinen Aktivitäten und des A^{40}-Gehaltes in Meteoriten sein. A^{40} ist bekanntlich in Luft zu 1% vorhanden, und es lässt sich nicht vermeiden, dass kleine Mengen während des Aufschluss- und Reinigungsprozesses in die Apparatur eindringen. Ausserdem müssten für Altersbestimmungen die Wirkungsquerschnitte auf der Isobaren 36 und 40 für hohe Energien noch genauer bekannt sein.

Die Deutsche Forschungsgemeinschaft hat diese Arbeit durch Sachbeihilfen unterstützt.

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Hydrogen-deuterium exchange in clays and problems in the assignment of infra-red frequencies in the hydroxyl region*

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(*Received* 30 *March* 1956)

Abstract—An examination of the "hydroxyl region" of the spectra of brucite, gibbsite, kaolin family minerals, and montmorillonites in various states of dehydration show the spectra to be much more complex than at first expected. The presence of multiple absorption bands even in powder spectra of minerals such as brucite, gibbsite, and the clay minerals, cannot yet be explained in terms of the X-ray structure. There is no simple correlation of OH^- absorption frequencies with "types of OH^-," and extent of hydrogen bonding, based on the data obtained. OD^- is shown to replace OH^- approximately equally in the three maxima in kaolinite and dickite in the 2·7-micron region, when the minerals are reacted with D_2O at about 370°C and 20,000 p.s.i. The more common generalization that hydrogen-bonded OH^- ions show a bathochromic shift compared to the "free" or "symmetrical" OH^- is also not borne out by our data, which show that, at least in part, the longer wavelength 2·9-μ maximum is the result of hydroxyls which remain in the structure of montmorillonite heated at elevated temperatures.

Deuterium-exchange experiments indicate that the exchange of hydroxyls varies widely with temperature. Attempts of 1-month duration to exchange OD^- for OH^- at room temperature indicated practically no exchange in dickite and kaolinite, with only a small amount in montmorillonite. Under elevated pressures, a significant amount of exchange was observed in kaolinite at 190°C, and extensive exchange took place in kaolinite at 370°C (greater than 50%), somewhat less in montmorillonite, and the least in dickite. In all the OD^- phases and in synthetic $Mg(OD)_2$, the OD^- absorption maxima are moved to greater wavelengths by a multiple of about 1·37 from the corresponding OH^- maxima in the original minerals.

Introduction

Anion exchange in clay minerals has been the subject of considerable investigation in recent years, and although it is generally accepted that the magnitude of exchange is less than that of cation exchange, the extent and mechanism of exchange is of considerable interest. Emphasis has been largely on the substitution of phosphate for OH, and more recently on the replacement of OH^- by the similar-sized F^- ion. The anion most similar to OH^- is, of course, OD^-. And while it is recognized that the actual mechanism of exchange taking place in the presence of OD^- is most probably $H^+\langle - - \rangle D^+$, the exchange measured in terms of OD^- replacement may well set a maximum on the amount of true anion exchange realizable under the given conditions. Because of the large differences between the infra-red absorption frequencies of equivalent OH^- and OD^- containing compounds, infra-red absorption spectra should serve as a sensitive indicator of OH^--OD^- exchange.

Among the considerable amount of work on phosphate exchange is that of Buswell and Dudenbostel (1941), who found by means of infra-red absorption studies that the amount of OH^- in the clay decreased on treatment with phosphate; but no evidence exists at the same time for the actual mechanism of

* Presented at the Fourth National Clay Conference, University Park, Pa., 10–13 October 1955.
† Contribution No. 55-48.

the exchange and the final site of the phosphate ion. Dickman and Bray (1941) and later Romo and Roy (1954) studied F^--OH^- exchange, and the latter authors attempted to find by the use of several techniques how the OH^- is replaced by F^-. Because NaF was used as the source of F^-, decomposition of the clay structure could be detected by the precipitation of cryolite—and in most cases removal of Al from the kaolinite lattice was thereby indicated. No positive X-ray evidence was found to establish entry of F^- into the lattice, although three separate methods indicated "exchange" of F^- from liquid to total solid.

McAuliffe *et al.* (1947) studied "OD^- exchange" with various minerals, indicating that at room temperature the amount of exchange is roughly correlatable with surface hydroxyl in kaolinite, determining the magnitude of exchange by liquid density measurement, which gives, however, no direct evidence as to the actual role of OD^- in the solid phase-structure.

The present study of OH^--OD^- (or H^+-D^+) exchange was undertaken using the infra-red absorption spectra for detection of extent of exchange. At the same time it was expected to obtain further information on the infra-red spectra of the minerals investigated. During the past several years a considerable amount of work has been done on the infra-red spectra of various clays, including that of Adler, Bray, Stevens, Hunt, Keller, Pickett, and Kerr (1950); Keller and Pickett (1950); Launer (1952); Hunt *et al.* (1950). By and large, no significant correlations, in the hydroxyl region of the spectra, have emerged from this work. In the last year or two, however, detailed attention has been given to the O-H stretching region of the layer lattice minerals. Sutherland (1952) (see also Mara and Sutherland, 1953) has done extensive work in this field, particularly on micas and brucite, and Frederickson (1954) has produced beautifully resolved spectra of some alumina hydrates. In recent papers (Auskern and Grimshaw, 1955; Wadsworth *et al.*, 1955; Dietzel—see Hofmann, 1955) various authors have attempted to correlate the different bands in the OH^- region with different types of hydroxyl. Allied to this is the much earlier work of Buswell and Dudenbostel (1941), who attempted to correlate the H_2O and OH^- in a montmorillonite with 2·9- and 2·7-μ absorption maxima. The data obtained in the present study have necessarily shed some light on these problems and also on others.

Experimental

Materials used. Various natural and synthetic minerals were used under room temperature conditions or, where significant, dried at successively higher temperatures. Synthetic minerals included H_2O-kaolinite, montmorillonite, and saponite; their partially deuterated counterparts when synthesized in a bomb containing D_2O from gels containing some H_2O; D_2O-kaolinite synthesized from metakaolinite; and $Mg(OD)_2$. The D_2O was obtained from the Stuart Oxygen Company, 99·5% pure, although no confirmation of the analysis was made during its use.

Method of exchange. At room temperature the samples were put in individual vials with a weight ratio of about 4 : 1 D_2O to dried sample, and enclosed in a bell-type jar. Original attempts at exchange through the vapour phase yielded negative results. The hydrothermal apparatus used for synthesis and exchange has been described by Roy and Osborn (1952). Small gold- or silver-lined Morey-type bombs were used to contain the D_2O, and the pressure generated by the D_2O put in the sealed bomb was taken to be the same as that calculated from p.v.t. data for H_2O at the temperature of the experiment.

Examination of samples. The samples were identified at various stages by their X-ray diffraction patterns, obtained on the Norelco wide-range diffractometer. Infra-red absorption spectra were obtained on the Perkin-Elmer model 21 double-beam spectrometer, using an NaCl prism. Weighed amounts of sample were intimately mixed with KBr, pressed into a disc (using about 100,000 p.s.i. pressure), and used in conjunction with a reference disc of pure KBr.* In the case of clays dried above 200°C, the samples were transferred directly into the pellet mould with the KBr, and pressed as quickly as possible. Standard slit-width (continuously varied by the automatic slit-drive) was used for most of the spectra, although narrowing the slit-width was found advantageous in a few instances. For routine examination, the spectra were scanned at a speed of about $\frac{1}{2}$ micron per minute; some spectra were obtained at about $\frac{1}{5}$ micron per minute, or slower, particularly in combination with faster-chart speeds, which were used to spread out the spectra and obtain greater resolution and precision in measurement.

Spectra of hydroxide minerals. Table 1 gives a summary of the absorption frequencies observed in various hydroxide minerals. The principal region studied was that where O-H stretching vibrations occur, ca. 2–3·5 μ (5000–2860 cm^{-1}), but more complete spectra are given for goethite and groutite, which are presumably analogous to diaspore, and whose spectra do not occur in the literature. The brucite absorption frequencies (obtained with standard instrument settings) agree reasonably well with those given by Mara and Sutherland (1953) for single crystals, although the intensity of absorption is somewhat different. This comparison gives an agreement in absolute wavelength of about 0·03 microns, and may be used as a limit-of-error calibration of the method, although part of the difference may be due to differences in the powder vs. single-crystal methods.

Table 1. Powder infra-red absorption spectra† of typical hydroxides

Brucite 0·0075/0·25 g KBr	Gibbsite ~0·005/0·25	Boehmite ~0·005/0·25	Diaspore 0·004/0·25	Goethite 0·0075/0·25	Groutite 0·0075/0·25
2·33 w*					
2·47 m					
2·68 s	2·74 ms			~2·7 vw	
2·8 w	2·82 vs				~2·8 vw
	2·87 vs				
3·03 mw		3·0 } vs			
3·45 w	3·3 vw	3·14 } vs	3·4 ms, br.	~3·4 vw, br	~3·6 vw, br
3·96 w					
	4·6 vw	4·75 s	4·70 m		
	4·95 w	5·05 ms	5·02 m		
		5·55			
				9·05 w	9·72 s
					10·04 vs
				10·95 } vs	
				11·2 }	
				12·3 }	
				12·5 } vs	
				12·8 }	
				15·0 mw	

† Abbreviations: w = weak, m = moderate, s = strong, v = very, br = broad, } = indicates poor resolution of multiple band.

* In a typical case the blank KBr disc when run alone showed complete transparency except for a very weak broad absorption band at about 2·9 microns. When balanced against another blank, the pattern showed essentially complete transparency. Although the blank was not checked for each spectrum, a reference KBr blank was pressed each time new samples were pressed.

The spectra of the alumina hydrates are not very different from those of Frederickson (1954), although the resolution obtained with the double-beam instrument used in the present study is of course not as great. Spectra for goethite (FeO·OH) and groutite (MnO·OH) would be expected to be similar to that of the structural analogue, diaspore, but the spectra do not show a clear correspondence. The very weak maxima at 3·4 and 3·6 microns for goethite and groutite, respectively, follow the generalization that a strong degree of hydrogen bonding is reflected in a weak absorption maximum at a lower frequency. The other weak maxima at 2·7 and 2·8 μ, respectively, in the two minerals at first suggest the presence of a second type of OH^- in the structures.

Spectra of OH^- Clays

Table 2 summarizes the spectra in the low-wavelength region for a number of clay minerals at 225°C. Fairly good resolution of the kaolinite and dickite spectra

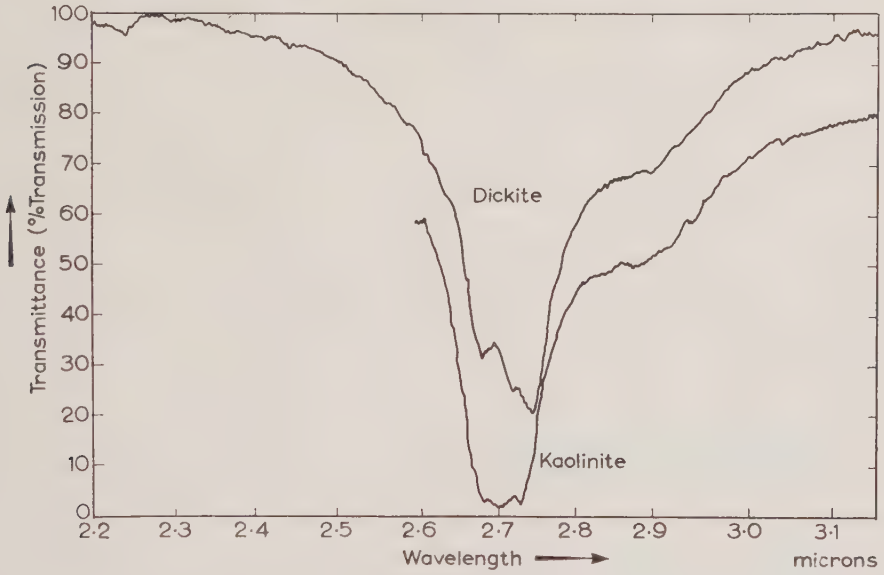

Fig. 1. Infra-red spectra of dickite and kaolinite obtained with slow-scanning speed showing resolution of maxima in OH^- region.

was obtained using a fast-chart speed and slow-scanning speed on the spectrometer. In Fig. 1 actual spectra for kaolinite and dickite are shown. Characteristic are the three distinctly resolved peaks for dickite in the 2·67–2·73-μ region, while the kaolinite pattern has two distinctly resolved with a third barely resolved, but which seems to be real and reproducible. The intensity patterns of the spectra are characteristic for the two species.

The spectra of talc and pyrophyllite appear to be very similar; but the overall intensity of the talc pattern is weaker than that for pyrophyllite, and the 2·91-μ peak is stronger relative to the 2·70-μ peak than in pyrophyllite. The presence of the 2·78-μ maximum in clinochlore (a relatively long wavelength) may not be significant, since it was not possible to grind the natural clinochlore down to a very fine particle size, and the spectrum may be modified by scattering effects. The presence of an absorption maximum at 2·9 μ in all the minerals in this table,

particularly when dried as high as 225°C, first suggests that this frequency cannot be assigned solely to "adsorbed" water.

Some of the spectra of Table 2 are represented in the form of block-type diagrams in Fig. 2, along with a similar representation for gibbsite and brucite. which gives a more convenient comparison of the intensity distribution and diagnostic features of the spectra.

Table 2. Infra-red spectra* of typical clays dried at 225°C

Kaolinite† 0·002 g/0·35 g KBr	Dickite† 0·002/0·35	Pyrophyllite 0·006/0·25	Talc 0·0055/0·25	Chrysotile 0·006/0·25	Hydralsite 0·006/0·25	Clinochlore 0·004/0·25
2·225 vw	2·225 vw					
2·678 ??}	2·673 s					
2·700 vs}	2·708 vs	2·71 vs	2·70 s	2·70 vs	2·72 s	
2·727 vs	2·732 vvs					2·78 vs
2·87–2·92 m,sh	2·89 m, sh	2·90 s–vs, br	2·91 s, br	2·91 br	2·89 m, br	2·92 vs
				3·40 vw	3·41 w	
		4·25 vw	4·3 vvw			4·3 vvw
		5·06 vw	5·2 w		5·3 vw	
		5·28 m	5·49 w			
		6·12 w	6·06 w	6·1 mw	6·2 vw	

* Abbreviations: w = weak, m = moderate, s = strong, v = very, br = broad, } = poorly resolved doublet, sh = shoulder.

† Spectra obtained with fast chart speed, scanning about 5 min/micron.

In Table 3 are given data from spectra of typical montmorillonite-type minerals heated at different temperatures, and some of the spectra are represented in the block diagrams of Fig. 3. The most important features to be observed are the relative heights of the 2·7- and 2·9-μ maxima. A comparison of typical air-dry montmorillonite with those dried at 250–300°C indicates a decrease in the height of the 2·9-μ maximum, but it nevertheless remains quite strong in all cases. This again suggests that the 2·9μ maximum cannot be entirely attributed to "interlayer water."

In synthetic Al-montmorillonite, i.e. the pure Al-Si beidellite end member, the 2·9-μ absorption apparently reached a "minimum" in the sample dried at 110°C (which is already collapsed at that temperature to a 9 Å basal spacing)—and the 2·9 peak has increased relative to the 2·7 on heating to 250°C. Nontronite consistently has its maximum at a longer wavelength than montmorillonite (e.g. 2·77 vs. 2·72), although the position of the peak may appear to be shifted by the presence of different amounts of interlayer water.

D_2O Exchange in Clays

Synthesis of standards. It was desired to synthesize end-member D_2O minerals to use as standards for determining the amount of D_2O exchange realized under various conditions. The most successful attempt was $Mg(OH)_2$, which was crystallized from MgO (calcined at 1400°C) at 375°C and 20,000 p.s.i. (D_2O). The

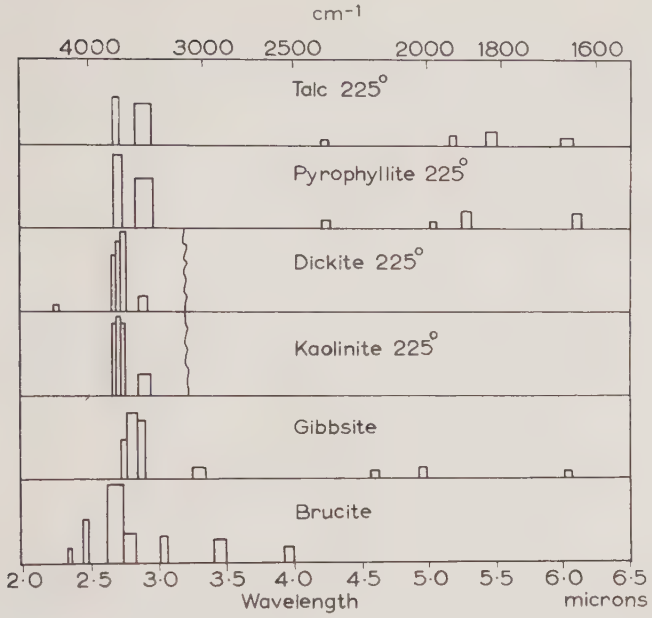

Fig. 2. Block diagram representation of clay and hydroxide spectra from Tables 1 and 2. Relative heights of blocks represent intensity of absorption, and widths correspond approximately to broadness of maxima. Actual spectra of dickite and kaolinite are in Fig. 1, and that of brucite in Fig. 4.

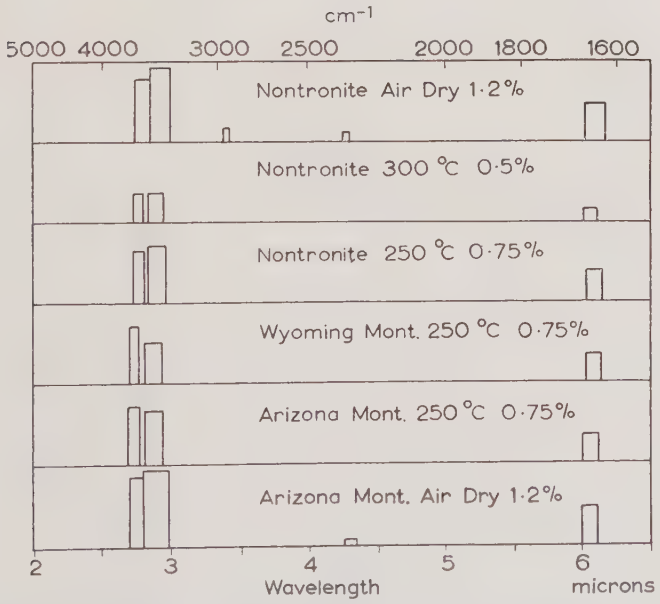

Fig. 3. Block diagrams of montmorillonites (OH) dried at various temperatures. Percentage refers to concentration of mineral in KBr disc.

Table 3. Infra-red spectra* of montmorillonites

Montmorillonite (Arizona) Dried: 250°C 0·002/0·25 g KBr	Nontronite Dried: 250°C 0·002/0·25	Montmorillonite (Wyoming) Dried: 250°C 0·002/0·25	Al-Montmorillonite (synthetic) Dried: 250°C 0·002/0·25	Nontronite Dried: 300°C 0·001/0·25
2·72 s	2·77 s	2·72 s	2·72 s	2·76 ms
2·88 s, br	2·89 vs, br	2·88 ms–s, br	2·88 s, vbr	2·90 ms
	3·38 vw			
6·07 ms	6·08 ms	6·08 m	6·1 m	6·07 m
Mont. (Arizona) Air-dried 0·003/0·25 g KBr	**Nontronite Air-dried 0·003/0·25**	**Synthetic Mont. Dried: 110°C 0·005/0·25**	**Synthetic Al-Mont Dried: 110°C 0·005/0·25**	
2·76 s	2·80 s	2·72 vs	2·71 vs	
2·91 vs	2·93 vs	2·91 vs	2·88 ms	
	3·4 mw	3·08 s		
	4·28 vw			
6·07 ms	6·1 ms	6·06 m	6·12 mw	

* Abbreviations: w = weak, m = moderate, s = strong, v = very, br = broad.

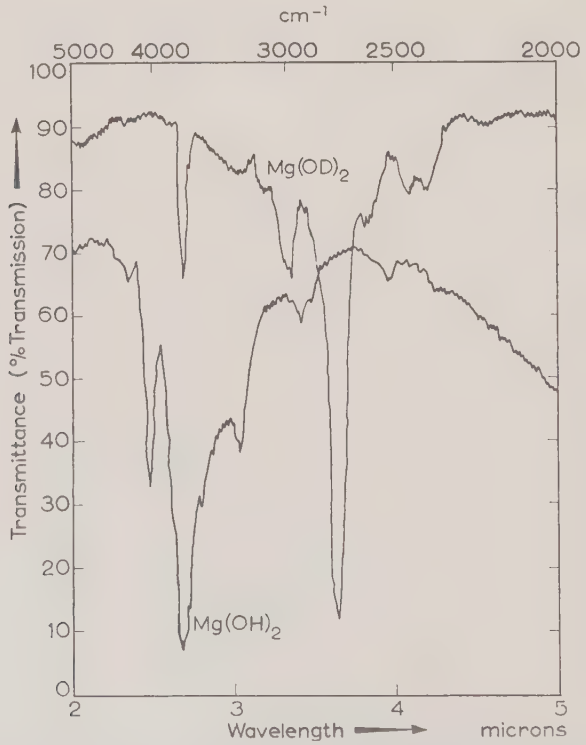

Fig. 4. Spectra of $Mg(OH)_2$ and $Mg(OD)_2$, using moderate scanning speed: The 2·68 μ maximum in the $Mg(OD)_2$ corresponds to OH^- impurity. Other maxima are shifted by the multiple 1·37 from those of $Mg(OH)_2$.

spectrum is given in Fig. 4 compared with that of $Mg(OH)_2$. The similarity is great, with at least five maxima being present in $Mg(OH)_2$ at multiples (1·37 times) of the corresponding OH wavelengths. A small amount of OH^-, however, is present in the D_2O phase.* The measured values of the $Mg(OD)_2$ spectrum are given in Table 4 along with other OD^- phases, and may be compared with the values for $Mg(OH)_2$ in Table 1.

Table 4. Spectra* of D_2O-containing phases exchanged or synthesized at elevated temperatures and D_2O pressures

$Mg(OD)_2$† tr $Mg(OH)_2$] 1 day, 375°C 20,000 p.s.i. Dried: 225°C	Kaolinite Exchanged 1 day, 370°C 20,000 p.s.i. Dried: 275°C	Kaolinite‡ Exchanged 2 days, 365°C 20,000 p.s.i. Dried: 225°C	Kaolinite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 300°C	Dickite Exchanged 1 day, 370°C 20,000 p.s.i. Dried: 275°C	Dickite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 300°C	Montmorillonite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 300°C
2·68 mw (OH)	2·71 vvs	2·72 sm	2·715 ms	2·69 ms–s	2·685 ms	
				2·72 s }	2·72? s }	
3·04 vw	2·74 vs	2·740 m	2·74 ms	2·75 vs}	2·745 vs}	2·745 s–vs
3·18 vw	2·9 m, br	2·90 mw, br	2·9 m, br	2·9 w, br	2·9 w, br	2·90 vs, br
3·35 m	3·42 vw	3·42 w	3·42 vvw		3·42 vw	3·41 w
3·65 s	3·665 vs}	3·660 vs}	3·655} –vs	3·65 w	3·66 mw	
	3·68? }	3·68? vs}	3·68?}			
3·84 vw	3·73 s	3·725 s	3·72 ms–s	3·725 mw}	3·72 mw–m}	3·715 m
4·08 w				? }	3·735 m }	
4·2 w, br						

Kaolinite Exchanged 22 days, 190°C 20,000 p.s.i. Dried: 110°C	Metakaolinite‡ Resynthesized 4 days, 360°C 20,000 p.s.i. Room Temp.	Metakaolinite† Resynthesized 4 days, 360°C 20,000 p.s.i. Dried: 110°C	Kaolinite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 110°C	Kaolinite Exchanged 29 days, 375°C 20,000 p.s.i. Dried: 110°C	Dickite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 110°C	Montmorillonite Exchanged 3 days, 370°C 20,000 p.s.i. Dried: 110°C
					2·685 ms	
2·72 vs	2·725 m}	2·71} vs	2·715 ms	2·725 mw	2·72? s }	2·755 vs
2·76 s	}	2·74}	2·74 ms		2·745 vs}	
2·92 w	2·9 ms }	2·86 s	2·9 m–ms, br	2·92 mw	2·9 w, br	2·90 vs, br
	3·39 w					
2·67 m	3·643 vs}	3·64 vs	3·66 vs }	3·66 s }	3·66 w }	
	3·67? vs}	3·68 vs	3·685 s–vs}	3·68 ms–s}	}	3·725 ms
					3·72? mw}	
3·74 mw–m	3·71 s		3·73	3·73 ms	3·735 m }	

* Abbreviations: of intensity of absorption: w = weak, m = moderate, v = very, s = strong, br = broad, } = refers to poorly resolved doublet.

† Concentration of samples were 0·0075 g/0·25 g KBr; all others were 0·001 g/0·35 g KBr.

‡ Sample using fast chart, scanning 5 min/micron.

Attempts were made to synthesize a pure D_2O kaolinite. Gels as starting material contained too much H_2O, so metakaolinite (heated at 800°C for 24 hours and transferred directly to the bomb) was used as a starting material. The product of synthesis was dominantly a D_2O kaolinite, containing OD^- maxima at 3·643, 3·67, and 3·705 μ; but also contained a fair amount of OH^- absorption in the

* It is difficult to determine exactly how much should be ascribed to the HDO present in the D_2O (99·5% pure).

2·7–2·9-μ region. Spectra for the resynthesis product are given in Table 4 in comparison with exchange products, and in block diagram form in Fig. 5.

Estimation of D_2O content of products. Inasmuch as neither a pure D_2O-kaolinite or montmorillonite had been synthesized to use as a reference standard, some assumptions were made in estimating the content of D_2O in a given phase. Although the $Mg(OD)_2$ contained a little OH^- also, the principal OD^- maximum had very nearly the same intensity as the OH^- principal maximum in brucite, and it is therefore assumed that, for a weighed quantity of sample, the intentities of absorption maxima for OH^- and OD^- are approximately the same.

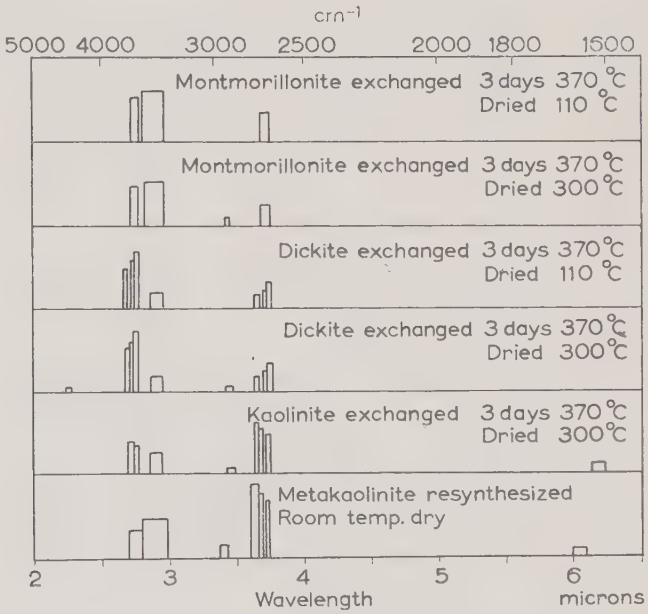
cm⁻¹
5000 4000 3000 2500 2000 1800 1600
Montmorillonite exchanged 3 days 370°C Dried 110°C
Montmorillonite exchanged 3 days 370°C Dried 300°C
Dickite exchanged 3 days 370°C Dried 110°C
Dickite exchanged 3 days 370°C Dried 300°C
Kaolinite exchanged 3 days 370°C Dried 300°C
Metakaolinite resynthesized Room temp. dry
2 3 4 5 6
Wavelength microns

Fig. 5. Block diagrams of clay spectra after D_2O exchange at elevated temperatures. These may be compared with original OH^- clays in Figs. 2 and 3.

Employing a dilution and sample split technique, the OH^- frequency* in concentrations of kaolinite as low as 0·00005 g/0·35 g KBr showed a moderate intensity; it is assumed that OD concentrations of similar magnitude would be easily detected also Samples of 0·001/0·35 or greater were usually used, and therefore OD concentrations of as little as 0·5% (in total OH +OD) should easily be detected.

Room-temperature exchange. Samples of kaolinite, dickite, and Arizona montmorillonite were dried at 300°C to eliminate all but the hydroxyl water, then treated with D_2O with a ratio of about 4:1, D_2O: clay by weight, at room temperature for 4 days. Spectra obtained for samples after the D_2O treatment and dried at 110°C and 300°C are summarized in Table 5. No detectable OD^- was observed

* The sharp OH^- absorption near 2·7 μ, even when very small, cannot be confused with "adsorbed" water on the KBr, which—as described earlier—only appears as a very weak broad 2·9 μ absorption, and in the double-beam technique is cancelled by similar absorption in the blank prepared from the same KBr at the same time.

in either kaolinite or dickite under these conditions of treatment, and hence it is considered that OD^- is present to the extent of less than 1% (of total $OH^- + OD^-$). Kaolinite treated for 1 month at room temperature had only a very slight indication of an absorption maximum at 3·7 μ, which would still indicate less than 1% OD^- present in the structure.

Montmorillonite dried at 110°C did not have the characteristic OD^- frequency, whereas, surprisingly, the sample dried at 300°C had a small maximum at 3·72 μ

Table 5. Infra-red spectra* of clays exchanged with D_2O at room temperature (2–4-micron region)

Kaolinite		Dickite			Montmorillonite	
Dried: 110°C	Dried: 315°C	Dried: 110°C† (29 days exchange)	Dried: 110°C	Dried: 315°C	Dried: 110°C	Dried: 315°C
2·22 vvw	2·22 vvw		2·22 vvw	2·22 vvw		
2·69 vvs	2·69 vvs	2·69, 2·74 vvs	2·67 s	2·675 s	2·74 vs	2·74 vs
2·73 vs–vvs	2·72 vs–vvs		2·71 s–vs, 2·725 vs	2·73 vs}		
2·86 mw, sh	2·87 mw, sh	2·9 w, sh	2·9 w, sh	2·88 m	2·91 vs–vvs	2·89 s–vs
3·42 vvw	3·41 vvw	3·4 vvw?		3·41 w	3·41 vvw	3·41 vvw
		3·7 vvw?		3·48 vw		3·72 w
		4·3 w				
					6·1 ms–s	6·1 ms

* Concentration of sample: 0·001 g/0·35 g KBr.
† Concentration of sample: 0·004 g/0·35 g KBr.
Abbreviations: w = weak, v = very, m = moderate, s = strong, sh = shoulder, } = refers to poorly resolved doublet.

indicating perhaps 2% OD^-. This may possibly be the result of some loosely-bound D_2O (giving rise to only a broad weak undetected absorption maximum) in the 110°C sample, which may, on heating to the higher temperature, actually be bound into the structure in a more regular manner.

No samples of montmorillonite in the room-temperature state were examined, partly because of the difficulty in maintaining "standard" conditions, and also because it seems obvious that exchange must take place in montmorillonite with the loosely held interlayer water,* and it was desired to avoid complications in the spectra as a result of molecular D_2O. The present results do indicate, however,

* Faucher and Thomas (1955) have recently studied the magnitude of D_2O exchange in air-dried kaolinite, montmorillonite, and other minerals, measuring the index of refraction of the liquid after exchange. Kaolinite was indicated to have no exchange at room temperature, within experimental error, and no significant amount at 200°C in a bomb for 1 day. Montmorillonite showed about 93% of total H_2O exchanged, but this is probably mostly interlayer and adsorbed water, as indicated in the present study. It is considered that the results of Faucher and Thomas in the low-temperature region are in good agreement with the present data.

that only extremely small amounts of true OH^--OD^- (or H^+-D^+) exchange take place in kaolinite and dickite at room temperature, and only a little takes place even in montmorillonite.

D_2O exchange at elevated temperatures and pressures. The same clays which showed a comparatively small amount of exchange at room temperature, when treated at elevated temperatures and pressures were found to exhibit a significant amount of exchange. Spectra obtained for typical samples are summarized in Table 4, and some of these are given in the block diagrams of Fig. 5. Kaolinite showed the greatest amount of exchange, more than 50% in 3 days, montmorillonite somewhat less than 50%, and dickite the least, although still a considerable amount. The effect of time is seen best in the kaolinite series at about 370°C, where exchange is greatest in 29 days, less in 3 days, and least in 1 day. The effect of temperature is also significant, as seen by comparison with the results at room temperature. Kaolinite treated for 3–4 weeks, at room temperature showed a very insignificant amount of exchange; at 190°C a considerable amount—about 10%; while at 370°C it is extensive, much greater than 50%.

In kaolinite and dickite the OD^- absorption maxima appear at wavelengths which are moved by the expected ratio of ca. 1·37 from those for the corresponding OH^- mineral, and in the same intensity pattern. Furthermore, the original OH^- frequencies decrease in the same ratios. In addition, the 2·94-μ maximum does not preferentially decrease, as would be expected if this were due to adsorbed H_2O. In montmorillonite the 2·74-μ OH^- frequency diminished with increase in the corresponding 3·72-μ OD^- frequency, but the 2·9-μ maximum remains particularly strong, and no D_2O frequency appears at the corresponding multiple.

Discussion

There is at present no simple correlation possible between the absorption frequencies in the O-H region of the infra-red pattern and the X-ray structure of the minerals studied. In the case of brucite this has been recognized by Mara and Sutherland (1953)—on the basis of single-crystal infra-red spectra. Even in the powder spectrum, however, there are not less than six separate frequencies, and the X-ray space-group requires equivalence of OH^-. Reconfirmation of the X-ray structure of brucite and the isomorphous structure portlandite have recently been completed by Petch and Megaw (1954), and a difference electron density-map constructed by Petch (1955). These show that the discrepancy cannot be explained by assuming a different structure. The same conclusion must be drawn from the data on gibbsite and some of the clays described herein, although the structures are not known to the same degree of precision as is the brucite structure.

On the basis of the brucite example, the correlation of absorption frequencies with structures of clays should be expected to be difficult. The assumption that a doublet in the absorption band of kaolinite at ca 2·7 μ corresponds to "inner" and "outer" hydroxyls in the kaolinite structure, i.e. those hydroxyls near and far from the silica sheet (Auskern, 1955; Wadsworth,1955; Dietzel (Hofmann, 1955) has been tested in the present study. In the first place, dickite and kaolinite both show three maxima in the 2·7-μ region, which adds to the complexity. As

OD^- is substituted for OH^-, the maxima decrease, maintaining their original intensity ratios, and the OD^- frequencies increase according to a similar intensity pattern. This is further evidence that the major absorption frequencies cannot be correlated with "inner" and "outer" hydroxyls, since the "outer" OH^- should diminish and the "outer" OD^- frequency should increase more rapidly than the inner counterparts.

To correlate strength of hydrogen bonding with position of the OH^- absorption frequency, such as has been done by Rundle and Parasol (1953), Lord and Merrifield (1953), Hartert and Glemser (1953), is very difficult in the case of crystalline solids. It has been generally assumed that the shortest O—O distances in hydroxy-minerals are caused by a strong degree of hydrogen bonding; the above results suggest that steric considerations may play a vital role in the determination of interatomic distances, and therefore the measured X-ray distances may not necessarily be correlatable to the nature of hydrogen or hydroxyl bonding. There is a general trend toward broad and weak lower frequency absorption bands for crystalline hydroxides or hydrates with a strong degree of hydrogen bonding, such as has been observed in many organic liquids, but the complexity of spectra caused by the much more complex bonding in solids renders difficult their interpretation, and exceptions do appear. In a crystal such as brucite, where there are several absorption maxima, one may well ask which one should be chosen for correlation with O—O distances. The same difficulty exists in the alumina hydrates, and in structures such as the clays which are not known with the same precision as the simple hydroxides such a correlation is even more uncertain. The persistence in samples heated to above 300°C of an absorption maximum at about 2·9 μ, particulary in montmorillonite, but also to a lesser extent in kaolinite and dickite, would have to be taken to indicate either that there is some H-bonded OH present in the structure at higher temperatures, or that the longer wavelength of absorption cannot always be correlated with hydrogen-bonding.

With respect to exchange phenomena, it has been established on the basis of infra-red absorption spectra, that less than 0·5% of the OH^- in the kaolin minerals is exchanged at room temperature in a few days. Since the mechanism of OH^--OD^- exchange is most probably proton-deuteron exchange, it is unlikely that true exchange involving entering the lattice of the original mineral can exceed this amount for other anions such as F^- or PO_4^{3-}. McAuliffe *et al.* (1947) indicated that essentially all the surface OH^- of kaolinite was replaced by OD^- in periods from a few days to months, on the basis of liquid-density measurements. This amount of OD^- (about 2–4%) is within the limit of detection by the infra-red absorption method used in the present study. The discrepancy may possibly be explained in terms of conditions necessary to give rise to characteristic infra-red absorption frequencies. It may be concluded that if the amount of exchange suggested by McAuliffe actually does take place, the OD^- is not sufficiently ordered in the structure to give sharp OD^- absorption bands at the expected frequencies.

Isotopic exchange in geological processes has recently become a subject of great interest. Although at room temperature experimental evidence for extensive

H-D exchange cannot be obtained, the exchange at elevated temperatures and pressures even in 1–3 days is extensive—greater than 50% in kaolinite, and increases further in a period of 1 month. Moreover, this is definitely exchange into a deuterium-clay lattice, with OD^- playing a similar role in the structures to that of the original OH^-. For all intents and purposes, therefore, exchange will probably be complete in a relatively short time under similar p.t. conditions. Particularly, given geological time, it would appear that the H-D ratio of a mineral would respond to changing isotope conditions in the water. Firstly, therefore, it appears that in isotope fractionation studies, the H-D ratio of clay-type minerals and very probably of other hydrous minerals cannot be used as a reliable guide to isotopic composition of the most ancient waters. Juvenile water passing through an environment of hydrous minerals on the way to the surface would similarly adjust itself to the H-D ratio prevailing in these early-formed minerals. Secondly, considerations of the origin (whether juvenile or recycled) of water in various geological environments based on the H-D ratio must reckon with the phenomenon of exchange between hydrous minerals and water, which has been demonstrated to be fairly rapid in clays. Especially in cases other than ground-water studies, such as in hot springs, it is quite clear that rapid mutual adjustment of H/D ratio must take place between the minerals present and the water moving up or down.

Acknowledgements—This work was carried out under the sponsorship of the American Petroleum Institute through a grant-in-aid from the ACFRORP committee (L. Laskaris, chairman).

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Zur Geochemie des Urans im Ostseebecken

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(*Received* 11 *February* 1956)

Abstract—In order to study the geochemistry of uranium on typical shelf zones, samples of river water and sea water, as well as samples of sediment from the Baltic Sea region, have been examined. The Baltic Sea region was chosen for the investigation since its hydrography is well known, water transport to and from it can be estimated to a high degree of accuracy, and the region can be well sampled.

The uranium content of river water originating in regions of igneous rocks is low, averaging $0{\cdot}5 \times 10^{-6}$ g U/l. The uranium content of rivers from sedimentary rock regions seems higher by a factor of two or more, the maximum value found being $12{\cdot}8 \times 10^{-6}$ g U/l. It may be concluded that the uranium is more easily leached out from sedimentary regions. While the southern and eastern rivers supplying water to the Baltic Sea have not been investigated, it can be assumed that their uranium content is high, especially since the sea area surrounding the mouths of these rivers exhibit high uranium values.

The radium content of river water is not in equilibrium with the uranium, amounting to only 10% of the latter. It is thus concluded that uranium is more soluble than radium.

The uranium content of water from the Baltic Sea is also variable, ranging from $0{\cdot}77$ to $5{\cdot}9 \times 10^{-6}$ g U/l. High salinity inflowing water shows $1{\cdot}8 \times 10^{-6}$ g U/l., while that of outflowing water is less, averaging $0{\cdot}9 \times 10^{-6}$ g U/l. Except for the southeastern regions and deep water areas, a marked correlation of salinity and uranium content exists. An increase of deep water uranium content correlates with a surface water increase. Surface water increases can be explained by the high uranium content of inflowing river waters; high deep water values are correlated with an oxygen deficiency. Here it may be assumed that the uranium (VI) is reduced to uranium(IV) forming insoluble complex compounds with organic material. This settles slowly to the bottom, and explains the rather high uranium content of the sediment (values range between $3{\cdot}2$ and $10{\cdot}3 \times 10^{-6}$ g U/g; the normal content in clays is about 2×10^{-6} g U/g). By an intense study of the distribution of uranium in sediments, completed by age determination by aid of carbon-14, it may be possible to follow the changes in the past of the state of ventilation of the deep basins of the Baltic Sea.

The attempt to work out a uranium balance sheet for Baltic Sea uranium demonstrates precipitation about equals that which is brought in by rivers. Influx totals 1100 to 1400 metric tons per year, efflux 700 to 1000, leaving about 100 to 700 tons of precipitated material.

The investigation carried out shows that a considerable quantity of uranium is precipitated on the Baltic Sea shelf. It appears to be caused by biological activity in the sea which in turn causes an oxygen deficiency. The process is slow. Rivers with a high uranium content can raise the uranium content of the sea water if they empty under conditions wherein the above factors are not fulfilled. On the other hand, in estuaries and bays into which uranium bearing rivers do not flow, uranium can be precipitated from sea water by a high biological activity, which is connected with oxygen deficiency. When the minerogenous sedimentation is at the same time very small, the uranium content of the sediment is enriched, amounting to 200×10^{-6} g U/g and more.

Die Geochemie des Urans scheint durch die verschiedene Löslichkeit des vier- und sechswertigen Urans bedingt zu sein. Außerdem spielt, wie Breger, Deul, und Rubinstein (1955) zeigen konnten, die Bildung unlöslicher, organischer Komplexe eine bedeutende Rolle. Uran wird in Sedimenten mit hohem Gehalt an organischer Substanz angereichert, besonders wenn sie marinen Ursprunges sind. Diese Anreicherung geht soweit, daß uranreiche Produkte wie Kolm in diesen Gesteinen gefunden werden. Strøm (1948) konnte auch zeigen, daß Uran in den Sapropelen der norwegischen Fjorde angereichert wird. Ebenso enthalten viele Ölschiefer Uran sowie Kupfer. Aber auch die Uranvorkommen nichtmarinen Ursprunges, die abbauwürdig sind, sind fast ausschließlich hydrothermaler Entstehung und man nimmt an (Bell in Faul, 1954), daß sie unterhalb der Oxydationszone abgesetzt

worden sind, auch wenn sie teilweise jetzt in der Oxydationszone gefunden werden. Betrachtet man den gesamten Urangehalt in der Hydrosphäre (Koczy in Faul, 1954; Holland und Kulp, 1954; Koczy, 1954), so ergibt sich, daß fast das gesamte mit den Flüssen transportierte Uran am Schelf abgesetzt werden muß, wenn man nicht annimmt, daß der Urangehalt des Meereswassers im Steigen ist, da man in den Tiefseesedimenten meist einen kleineren Urangehalt findet, als dem Durchschnittswert der Erde entspricht.

Die Ostsee, ein geschlossenes Meeresbecken mit einer schmalen Verbindung mit den Weltmeeren, stellt ein ideales Prüffeld dar, in dem der Mechanismus der Uranverteilung und -ausfällung verfolgt werden kann. Die geochemischen Verhältnisse in der Ostsee sind denen im Meere sehr ähnlich, doch ermöglicht die Begrenztheit der Ostsee eine leichtere Untersuchung. Die erhaltenen Resultate können dann ggf. für die geochemischen Betrachtungen über das Meer selbst nutzbar gemacht werden. Der Wasserhaushalt ist genau studiert (Wyrtki, 1954; Brogmus, 1952; u.a.) und ebenso ist die hydrographische Situation unter ständiger Kontrolle (Thomsen, Granquist, und Koczy in Ann. Biol. I. C.E.S.als Übersicht).

Die Proben für die Uranbestimmungen wurden im einströmenden wie im ausströmenden Wasser genommen. Desgleichen wurde ein Teil der zugänglichen Flußwässer untersucht. Im zentralen Gebiet der Ostsee wurden Wasserproben aus verschiedenen Tiefen sowie Sedimentproben aus den tiefsten Becken genommen. Einige Radiumbestimmungen in den Wasserproben runden das Bild ab.

1. Methodisches

1.1. *Probenahme*

Die Proben in den Flußwässern wurden von Beamten der schwedischen Fischereibehörde, denen an dieser Stelle unser Dank ausgesprochen sei, mit Hilfe von limnologischen Wasserschöpfern oder unmittelbar mit farblosen Einliter-Flaschen, in denen sie versandt wurden, geschöpft. Sofort nach der Entnahme wurden je 5 ml konz. Salzsäure (p.a.) zugesetzt. Die Glasflaschen mit den Proben wurden dann in Göteborg gesammelt und von dort in größeren Partien nach Wien versandt.

Die Meerwasserproben wurden mit den üblichen, innen verzinnten und mit Ceresin überzogenen Wasserschöpfern genommen, ebenfalls sofort in farblose Einliterflaschen gefüllt und mit der oben angegebenen Menge Salzsäure versetzt.

Alle Wasserproben (mit Ausnahme einer einzigen, vgl. Tabelle 2, Entnahmeort Bornö) wurden unfiltriert analysiert, da sie ganz klar waren und außerdem bei der Ätherextraktion (siehe unten) stark angesäuert wurden.

Die Sedimente wurden mit einer Einmeter-Stoßröhre aufgeholt. Aus jeder Röhrenprobe wurden einzelne Niveaus herausgeschnitten, von dem verschmierten Teil, der an der Prc-Röhre lag, gereinigt, dann in einem Pulverglas unter Verschluß aufbewahrt und schließlich versandt.

Sowohl die Seewasserproben als auch die Sedimentproben wurden von einem der Verfasser selbst (*K.*) vom Untersuchungsschiff "Skagerak" der schwedischen Fischereibehörde (Fiskeristyrelsen) genommen.

1.2. *Aufarbeitung der Proben*

Die Urananreicherung erfolgte mit Hilfe der schon 1939 und 1942 von Hecht und Korkisch (1939) bzw. Hecht und Grünwald (1942) angegebenen Ätherextraktionsmethode. Die Uranbestimmung wurde dann nach der Natriumfluoridperlenmethode ausgeführt (Hernegger und Karlik, 1935). Diese Analysenmethode wurde von Hahofer und Hecht (1954) im Zusammenhang mit der Uranbestimmung in Tiefseesedimenten genau beschrieben. Sowohl bei den damaligen Analysen als neuerlich in einer eingehenden Untersuchung der Mikromethoden zur Uranbestimmung (Hecht, Korkisch, Patzak, und Thiard, 1956), bei der vergleichsweise auch mit Ionenaustauscher und polarographischer Endbestimmung gearbeitet wurde, wurde in Standardlösungen bekannter, dem Meerwasser angeglichener Zusammensetzung eine maximale Abweichung der Uranmeßwerte um rund $\pm 10\%$ gefunden.

2. Analysenresultate

Sämtliche Proben wurden im Jahr 1953 gesammelt. Die Flußwasserproben wurden im allgemeinen in höchstens einigen Kilometer Entfernung von der Mündung geschöpft. Die Ergebnisse der Uranbestimmungen sind in Tabelle 1 nach Meeresgebieten angeordnet (vgl. Abb. 1).

Tabelle 1. Urangehalt von Flußwässern

Fluß	Datum der Probenahme	Bemerkung	Urangehalt in 10^{-6} g/l
Bottnischer Meerbusen:			
Torneälv	31 März	vereist	0,6
Torneälv	24 August		0,2
Luleälv	31 März	vereist	0,7
Luleälv	24 August		$0,2_4$
Skellefteälv	8 April	vereist	0,4
Indalsälv	Juli		$0,3_2$
Dalälv	23 April	Schmelzwasser	$0,6_6$
Kemiälv	Mai		$0,3_5$
Kumoälv	4 Mai		$0,6_3$
Finnischer Meerbusen:			
Kymmeneälv	1 Juni		$0,4_7$
Ostsee:			
Motala ström	18 April		$0,5_2$
Mörrumså	27 März		12,9
Öresund:			
Kävlingeå	31 März		1,4
Skagerak:			
Örekilsälv	21 September		0,5
Örekilsälv	21 September		$0,5_5$

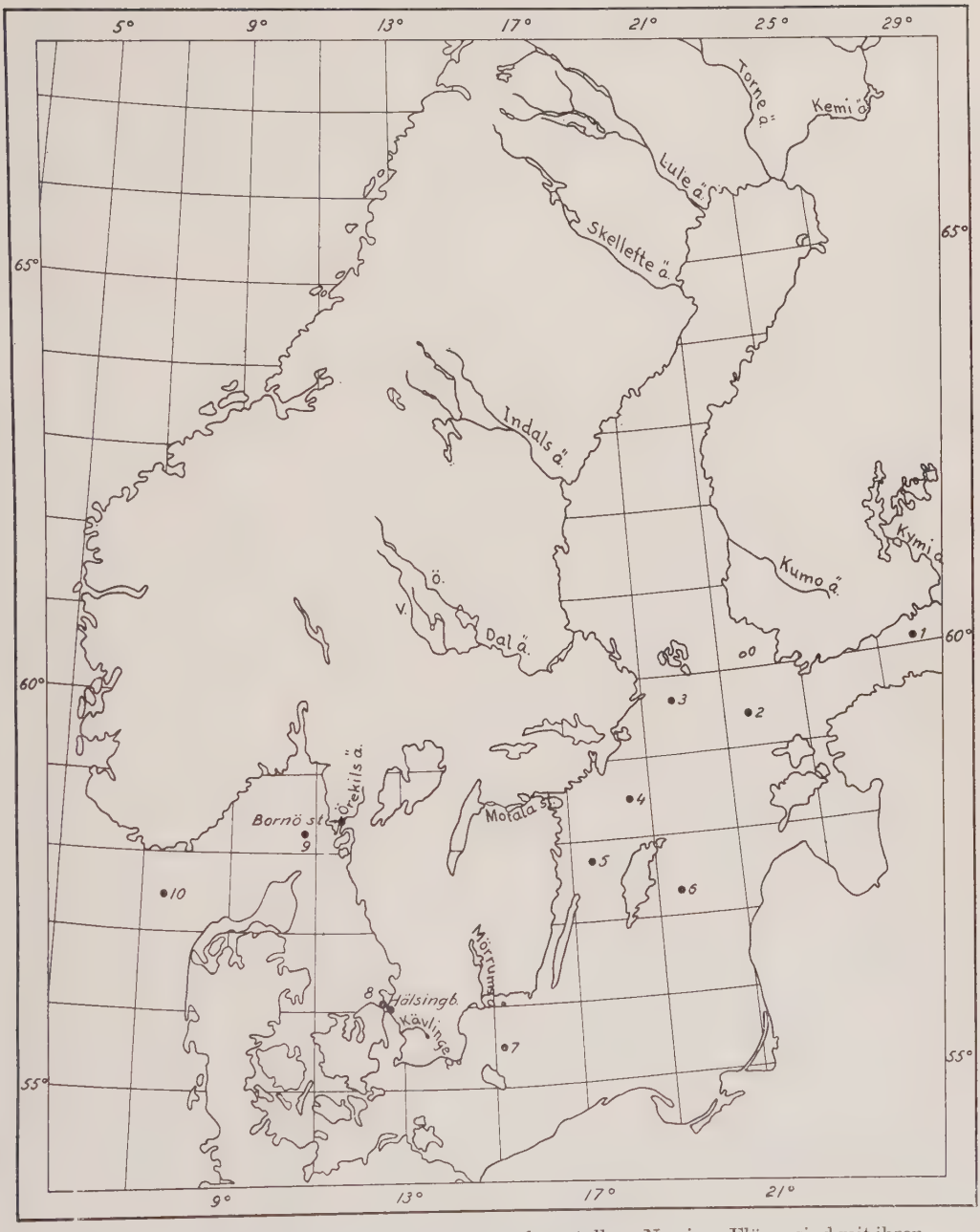

Abb. 1. Karte der Ostsee mit den Probenentnahmestellen. Nur jene Flüsse sind mit ihren Namen bezeichnet, an denen Proben entnommen wurden. Die Stellen an denen Meereswasserproben genommen wurden, sind in übereinstimmung mit der Tabelle im Texte numeriert

6A—(4 pp.)

Die Uranbestimmungen in Meerwasserproben sind in Tabelle 2 zusammengefaßt, wo auch die Positionen der Schöpfstelle angegeben sind. In Abbildung 1 sind diese Stellen mit Punkten gekennzeichnet.

Tabelle 2. Urangehalt von Ostseewasser und Skagerakwasser

Ort der Probenahme	Monat der Probenahme	Tiefe in m	Salzgehalt in Promille	Temperatur in °C	Sauerstoff in ml/l	Urangehalt in 10^{-6} g/l
Finnischer Meerbusen:						
7 Seemeilen (1) südlich Gråhamn	Juli	3	—	—	—	$0{,}7_7$
N 59°24′, E 21°36′ (2)	Juli	5	6,91	16,45	8,20	$0{,}7_7$
Ostsee:						
N 59°46′, E 19°47′ (3)	Juli	5	5,44	13	9	$0{,}8_0$
(Station F 69)		100	8,06	2,62	8	$0{,}8_5$
N 58°35′, E 18°14′ (4)	Juli	45	7,60	4,10	6	$0{,}9_5$
(Landsorttiefe)	Juli	455	11,67	5,40	1,50	$4{,}0_7$
	März	15	7,45	1,34	9,4	$0{,}8_7$
	März	430	11,40	5,12	1,2	$1{,}3_1$
N 57°46′, E 17°31′ (5)	Marz	5	7,16	0,99	9,63	$1{,}3_0$
	März	127	10,65	4,82	1,03	$1{,}2_0$
N 57°20′, E 19°54′ (6)	März	5	7,75	1,53	9,35	$1{,}9_0$
(Gotlandtiefe)	März	200	13,69	6,33	1,43	5,9
	Juli	40	7,76	3,30	8,27	2,0
N 55°32′, E 15°09′ (7)	März	5	7,50	2,18	9,70	2,2
(Bornholmtiefe)	März	75	16,65	5	2	1,1
Öresund:						
N 56°10′, E 12°30′ (8)	März	3	9,48	2,30		$1{,}1_3$
(Hälsingborg)	März	22	29,65	5,73		$1{,}8_3$
	Juli	5				$0{,}7_0$
	Juli	27				$1{,}8_5$
Skagerak:						
N 58°10′, E 10°51′ (9)	November	120	34,97			1,2
(Bornö)	November	15	32,2	11,85	filtriert	1,7
					unfiltriert	1,4

Die in der Tabelle 2 angegebenen hydrographischen Werte wie Salzgehalt, Sauerstoffgehalt und Temperatur wurden an Wasserproben bestimmt, die nicht mit dem für die Uranproben verwendeten Wasserschöpfer genommen wurden. Teilweise wurden die hydrographischen Proben auch aus anderen Tiefen geholt. In diesem Falle sind dann die in Tabelle 2 eingetragenen Zahlen interpolierte Werte. Kenntlich sind sie dadurch, daß die Dezimalen ausgelassen wurden. Besonders bei drei Proben wurde die Interpolation dadurch erschwert, daß sie nahe einer hydrographischen Grenzschicht genommen worden waren; daher war

es schwierig festzustellen, ob sie der unteren oder der oberen Wassermasse zugehörten. Die erste dieser Proben stammte aus 75 m Tiefe in N 55° 32′, E 15° 09′, wo gerade die Grenzschicht zwischen dem durch den Belt und den Sund einfließenden Wasser einerseits und dem im Ausfließen begriffenen Ostseewasser andererseits verläuft. Die zweite Grenzschichtprobe wurde in 5 m Tiefe in N 59° 46′, E 19° 47′ zwischen dem vom Finnischen Meerbusen ausfließenden Wasser und dem von Süden kommenden Ostseewasser genommen. Die dritte Probe wurde knapp oberhalb der Wassermasse, die nicht an der Winterzirkulation teilnimmt, in 45 m Tiefe in N 58° 35′, E 18° 14′ geschöpft.

Tabelle 3. Urangehalt von Sedimenten

Ort der Probenahme	Monat der Probenahme	Wassertiefe in m	Abstand von der Sedimentoberfläche in cm	Urangehalt in 10^{-6} g/g
N 58°35′, E 18°13′ (Landsorttiefe)	März	445	0 bis 1	5,1
			1 bis 3	$6{,}0_5$
			8 bis 10	3,8
			38 bis 40	2,2
N 57°20′, E 19°54′ (Gotlandtiefe)	März	215	0 bis 2	4,4
			8 bis 10	10,3
			24 bis 26	5,6
N 57°46′, E 17°31′	März	135	0 bis 2	4,6
			8 bis 10	3,6
			24 bis 26	2,6

Die Ergebnisse der Uranbestimmungen in den Sedimenten sind in Tabelle 3 zusammengefaßt. Da alle Sedimentproben aus dem sauerstoffarmen Teil der Tiefbecken in der Ostsee genommen wurden, sind sie ihrem Charakter nach Halbfaulschlämme. Sie zeigen großen Schwefeleisengehalt, sind schwarz gefärbt und riechen deutlich, manchmal sogar stark, nach Schwefelwasserstoff. Ihr Gehalt an organischer Substanz ist sehr hoch. Der oberste Teil, der mit Wasser stark vermischt ist, zeigt flockiges Aussehen.

Radiumbestimmungen in einigen der Wasserproben wurden im Ozeanographischen Institut in Göteborg von V. Kröll ausgeführt (s. Abschnitt 6). Sie wurden nach der dort üblichen, seinerzeit von Føyn, Karlik, Pettersson und Rona (1939) angegebenen Methode bestimmt. Die Genauigkeit der Bestimmung liegt bei den verwendeten Wassermengen von 20 Liter bei $\pm 0{,}5.10^{-14}$ g Ra/l.

Die Radiumproben wurden gleichzeitig mit den Uranproben genommen. Die entsprechenden hydrographischen Daten sind aus den Tabellen 1 und 2 zu entnehmen.

3. Die hydrographischen Verhältnisse in der Ostsee

Das der Ostsee *zufließende* Wasser ist dreifachen Ursprunges, während in zwei Richtungen Wasser *abgegeben* wird. Die totale Wasserbilanz ist mit den meteorologischen Verhältnissen sehr variabel. Mittelwerte für den Wasserhaushalt

wurden von Brogmus (1952) neu berechnet. Nach dessen Angaben liefern die Flüsse etwa ein Drittel der gesamten Wasserzufuhr; die Niederschläge betragen 13%. Dieser Süßwasserzufuhr steht eine Salzwasserzufuhr vom Kattegatt gegenüber, die 53% der Gesamtzufuhr ausmacht. Der Wasserverlust verteilt sich mit 13% auf die Abdunstung im ganzen Ostseegebiet, während 87% durch den Belt und den Öresund in den Kattegatt fließen. Man sieht somit, daß Niederschlag und Abdunstung in der Ostsee einander genau die Waage halten, wenn man einen langjährigen Durchschnitt berechnet. Dagegen mischen sich die

Tabelle 4. Radiumgehalt von Wässern des Ostseegebietes

Ort der Probenahme	Monat der Probenahme	Wassertiefe in m	Radiumgehalt in 10^{-14}g Ra/l
Flusswasser:			
Indalsälv	Juli		0,0 ± 0,5
Örekilsälv	November		1,8 ± 0,5
Ostseewasser:			
Station F 69	Juli	5	1,2 ± 0,5
		100	4,6 ± 0,5
N 59°24′, E 21°36′	Juli	5	5,2 ± 0,5
Landsorttiefe	Juli	45	2,0 ± 0,5
		445	4,7 ± 0,5
Gotlandtiefe	Juli	40	6,0 ± 0,5
		220	2,8 ± 0,5
Hälsingborg	Juli	5	1,2 ± 0,5
		27	4,5 ± 0,5

737 km³, die jährlich vom Kattegatt kommen, mit 479 km³ Süßwasser von den Flüssen. Dieses Mischwasser hat einen Salzgehalt von etwa 20‰ das einströmende Wasser von 33‰. Bei dieser Berechnung ist die Beltsee einbezogen worden.

Wird die Grenze mehr gegen die Ostsee zu verschoben, so enthält das einströmende Wasser 18‰, das ausströmende 9‰. Die Flußwasserzufuhr verringert sich sehr wenig, nämlich auf 472 km³, dagegen wird der Einstrom kleiner und zwar genau so groß wie die Flußwasserzufuhr, d.i. 472 km³. Der gesamte Ausstrom ist dann 944 km³. Daß dieser Mischungsprozeß kein kontinuierlicher ist und große Spitzen im Zufluß vorkommen können, wurde eingehend von Wyrtki (1954) gezeigt. Maßgebend für diese Variationen ist letzten Endes die Luftdruckverteilung über dem Gebiet. Wyrtki erhält auf Grund seiner Analyse auch einen größeren Wasserwechsel durch die Belte und den Sund.

Das salzreiche, vom Skagerak und dem Kattegatt kommende Wasser senkt sich, wenn es die Schwellen der Ostsee überschritten hat, infolge seiner größeren Dichte in die größeren Tiefen und erfüllt die Tiefbecken. Es breitet sich dann nach Nordosten aus, wobei sich durch Brackwasserzumischung aus der Oberflächenschicht sein Salzgehalt verringert. Die Grenzschicht zwischen diesem Bodenwasser und der

Oberflächenschicht wird meist zwischen 40 und 60 m Tiefe gefunden. Während des Winters wird die Oberflächenschicht durch thermische Konvektion gut gemischt, wodurch das Flußwasser gründlich in dieser Schicht verteilt wird. Im Sommer dagegen bildet sich infolge der Erwärmung der obersten Schicht eine Temperaturschichtung aus. Die Dicke dieser Schicht wächst von Juni bis Oktober und beträgt dann meist 20 m. Das Oberflächenwasser fließt hauptsächlich im westlichen Teil der zentralen Ostsee nach Süden und verläßt dann die Ostsee durch den Sund sowie den Großen und Kleinen Belt. Dabei nimmt der Salzgehalt langsam zu. Dieser ist somit ein Indikator für das Mischungsverhältnis von Flußwasser und reinem Meerwasser. Hier sei aber nochmals erwähnt, daß der Salzwassereinstrom diskontinuierlich verläuft, wie schon O. Pettersson (1908) und Schulz (1938) zeigen konnte und neuerdings von Wyrtki (1954), Wattenberg (1941) und Kändler (1952) nachgewiesen wurde.

Betrachtet man die Volumsverhältnisse, die dem einströmenden Wasser zur Verfügung stehen, und andererseits diejenigen, von denen das ausströmende Wasser gespeist wird, so ist es notwendig, von den Schwellen der Ostsee (Belt und Sund) abzusehen und die Grenze für unsere Untersuchung noch weiter nach Osten zu legen, wo auch die Salzgehaltverhältnisse stabiler sind. Hier ist der Salzgehalt des ausfließ, enden Wassers 7,5‰ und der des zufließ enden 15‰. Rechnen wir nun mit der zentralen Ostsee und nehmen an, daß die Deckschicht 40 m tief ist, so ergibt sich ein Volumen von ungefähr 7.10^{12} m³. Das Tiefenwasser ist schwerer abzuschätzen, soll aber hier gleichfalls mit 7.10^{12} m³ angenommen werden. Die Deckschicht, die jedes Jahr durch die Winterkonvektion gut durchmischt wird, wird durch den Zufluß von Flußwasser und die Zumischung salzreicheren Wassers von der Bodenschicht durchschnittlich jedes achte Jahr erneuert. Dagegen wird die Bodenschicht erst in der doppelten Zeit durch Salznachschub vom Kattegatt erneuert. Diese Zeiten stellen also die durchschnittlichen Verweilzeiten des Wassers in den betreffenden Schichten dar. Da sowohl die Größe des Zustromes als auch das Volumen der Bodenschicht sehr unsicher sind, ist der Wert für die Bodenschicht ungenau. Man kann aber annehmen, daß die Zeit eher zu klein als zu groß geschätzt wurde.

4. Der Urangehalt des Zuflusses

4.1. *Flußwasser*

Seit die Übersicht über Uranbestimmungen in dem Sammelband von Faul (1954) erschienen ist, wurden in den Vereinigten Staaten von Amerika neue Bestimmungen veröffentlicht (Judgon und Osmond, 1955; Adams, 1954). Diese Werte bewegen sich zwischen $0{,}1.10^{-6}$ und 20.10^{-6} g U/l. Der wahrscheinlichste Wert des Urangehaltes kann aus dem geometrischen Mittel erhalten werden und liegt bei $0{,}6.10^{-6}$ g U/l. Dagegen ist der Mittelwert, der allein für Bilanzrechnungen in Frage kommt—selbstverständlich sollten dabei die Gewichte des Wassertransportes mit ins Kalkül gezogen werden—, etwas höher und liegt bei $1{,}1.10^{-6}$ g U/l.

Die Werte, die wir in den von uns untersuchten Proben fanden, sind von derselben Größenordnung wie die neuen amerikanischen Werte. Der geometrische

und der arithmetische Mittelwert nähern sich einander sehr, was auf kleine Streuung deutet. Die Mittelwerte sind in Tabelle 5 zusammengefaßt.

Die kleine Anzahl der von uns untersuchten Proben läßt noch keine endgültigen Schlüsse zu. Immerhin kann aber gesagt werden, daß die nördlichen Flüsse, die aus dem Grundgebirge reich an Granit und Gneis, kommen, sehr kleine Uranwerte aufweisen. Dasselbe gilt für den Örekilsälv. Dagegen zeigt der Kävlingeå eine höhere Urankonzentration, die vielleicht mit dem kalkreichen Milieu und dem höheren pH-Wert in Zusammenhang gebracht werden kann. Der einzige herausfallende Wert wurde beim Mörrumså gefunden. Da von dort nur eine einzige Messung vorliegt, muß man hier mit den Schlußfolgerungen vorsichtig sein. Trotzdem neigen wir zu der Ansicht, daß dieser Wert reell ist. Die Ursache wird in nächster Zeit untersucht werden, wobei der Urangehalt des ganzen Flußlaufes kontrolliert werden soll.

Tabelle 5.

Probenzahl	10^{-6}g U/l	
	geomet. Mittel	arithmet. Mittel
Flüsse des Bottnischen Meeres: 10 Wässer	0,42	0,46
Alle untersuchten Flüsse: 15 Wässer	0,94	1,03

Bei den Flüssen, die während zweier verschiedener Jahreszeiten untersucht wurden, ergab sich ein systematischer Unterschied. Der Sommerwert ist kleiner als der Wert vor der Schneeschmelze. Das kann mit der Wasserführung der Flüsse zusammenhängen, würde aber in diesem Fall bedeuten, daß die Auslaugung des Urans während des Jahres mehr oder weniger konstant und unabhängig von der transportierten Wassermenge ist. Das könnte so erklärt werden, daß trotz steigendem Grundwasserspiegel vom durchsickernden Regenoder Schmelzwasser nicht sehr viel mehr Uran herausgelöst würde, das Flußwasser also bei zunehmender Wasserführung eine niedrigere Urankonzentration aufwiese.

Da die polnischen und russischen Flüsse nicht untersucht wurden, ist es sehr schwer, die Uranmenge abzuschätzen, die jährlich durch Flußwässer in die Ostsee gebracht wird. Die geologischen Verhältnisse in den östlichen und südlichen Ländern des Ostseegebietes erinnern aber vielfach an die des südlichen Schwedens. Es ist daher anzunehmen, daß hier hohe Uranwerte vorherrschend sind.

4.2. *Meereswässer*

Die Messungen in Wässern im Öresund zeigen, daß das einströmende Meerwasser einen höheren Urangehalt als die Flüsse aufweist. Der mittlere Gehalt entspricht $1{,}85.10^{-6}$ g U/l. in Wässern mit ungefähr 30‰ Salzgehalt. Messungen in der Nordsee mit 35‰ Salzgehalt ergaben vorläufige Werte von 1.5 bis $1{,}9.10^{-6}$ g U/l., also in relativ guter Übereinstimmung mit den im Öresund erhaltenen. Dagegen sind alle Werte etwas höher als die von Føyn *et al.* (1939) angegebenen Uranwerte aus demselben Gebiet.

5. Der Urangehalt der Ostsee

Alle Wassermassen der Ostsee sind durch Mischprozesse aus Flußwasser mit ozeanischem Wasser entstanden. In den verschiedenen Teilen der Ostsee bilden sich typische Brackwässer, die durch ihren Salzgehalt charakterisiert sind. Mit Hilfe des Salzgehaltes kann man auch das Mischungsverhältnis berechnen. Der Chlorgehalt, auf dem die Salzgehaltbestimmung beruht, ist eine konservative

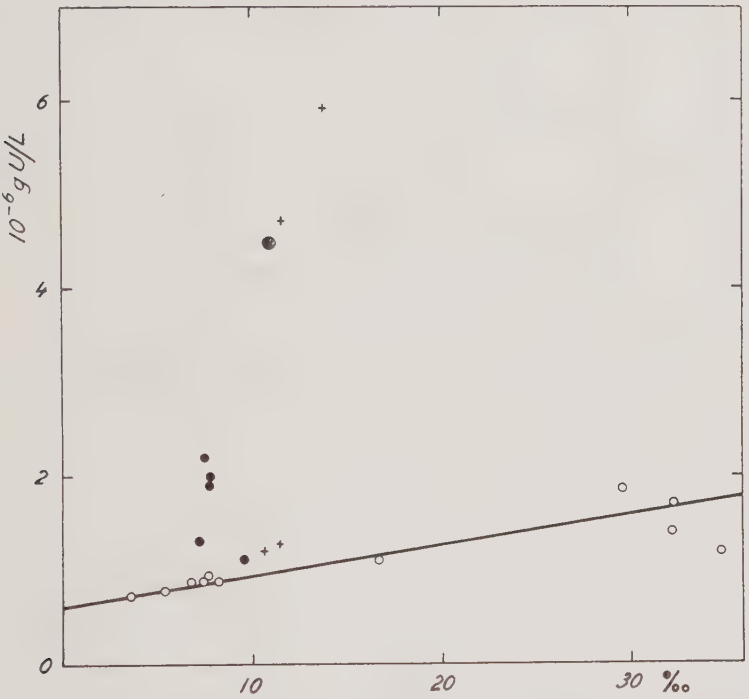

Abb. 2. Der Urangehalt der Wasserproben in Abhängigkeit vom Salzgehalt. Kreuze markieren die saustoffarmen Bodenwasserproben. Volle Ringe bezeichnen die Proben der südlichen und östlichen Ostsee. Leere Ringe bezeichnen alle übrigen Proben, also die Proben der nördlichen Ostsee und des Zu- und Abflusses.

Eigenschaft, die nicht durch chemische oder biologische Prozesse geändert wird. Wäre nun der Urangehalt der Flüsse und des Meeres konstant, dann sollte eine lineare Uran-Salzgehaltbeziehung gefunden werden. Abweichungen von einer solchen Beziehung lassen aber Rückschlüsse auf die geochemische Verteilung des Urans zu.

Betrachten wir die erhaltenen Uranwerte in ihrer Beziehung zum Salzgehalt (Abb. 2), so sieht man, daß für die meisten der Proben eine lineare Beziehung besteht. Die Gerade, die durch die Brackwasserproben gegeben ist, läßt auf einen Flutßwassergehalt von $0{,}6.10^{-6}$ g U/l. schließen, d.i. also auf einen etwas höheren Wert, als es der von uns für die nördlichen Proben erhaltene war. Der extrapolierte Wert für das reine ozeanische Wasser ergibt den gleichen Wert, den wir in Skagerakproben fanden, nämlich $1{,}85.10^{-6}$ g U/l. Die Ostseeproben, die also einen Urangehalt zwischen diesen beiden Grenzen in Übereinstimmung mit ihrem Salzgehalt

zeigen, stammen aus dem nördlichen Teil der Gotlandsee, wo das im Finnischen Meerbusen und im Bottenmeer gebildete Mischwasser in die Gotlandsee fließt. Die Proben aus der südlichen Ostsee dagegen weisen einen höheren Urangehalt auf, der bei 2.10^{-6} g U/l. liegt. Sie sind durch drei Stationen belegt, von denen eine sowohl im März als auch im Juli erhöhte Uranwerte lieferte. Diese Wässer sind ein Mischprodukt aus dem einfließenden Salzwasser mit ungefähr 18‰ Salzgehalt, den von Norden kommenden Wässern des Baltischen Stromes und den Flußwässern aus dem Süden. Da das Mischwasser der beiden erstgenannten einen Urangehalt Kleiner als $1{,}2.10^{-6}$ g U/l zeigt, muβ man annehmen, daβ die südlichen Flußwässer einen hohen Urangehalt aufweisen. Dieser Schluß wird erhärtet durch die Uranmessungen in den Flüssen des südlichen Schwedens und besonders des Mörrumså. Dieser eine Fluß kann aber nicht allein für die starke Erhöhung verantwortlich gemacht werden, da er jährlich nur 1 km³ Süßwasser der Ostsee zuführt.

Die höchsten Uranwerte wurden im Tiefenwasser der Gotlandtiefe und der Landsorttiefe mit einem Maximum von $5{,}9.10^{-6}$ g U/l. gefunden. Da dieses Wasser aus dem von den Belten und dem Sund kommenden Salzwasser, das auf seinem Weg zu diesen Tiefen durch Mischung mit Oberflächenwasser ausgesüßt wurde, gebildet ist, muß auch hier ein anderer Ursprung für die Urananreicherung gefunden werden. Eine Möglichkeit wäre die Annahme, daß das Uran aus dem Sediment ausgelöst und dadurch die tiefen Wasserschichten an Uran bereichert werden. In diesem Fall bleibt aber die Frage nach der Herkunft des uranreichen Sedimentes offen. Dieses müßte ja auch durch Flüsse transportiert werden und so deren Urangehalt beträchtlich erhöhen. Schließlich sollte es nach der Überführung in den gelösten Zustand doch allmählich in die Oberflächenschicht gelangen und deren Urangehalt erhöhen. Eine andere Möglichkeit ist, daß das Uran aus der Oberflächenschicht ausgefällt wird und so in die tieferen Wasserschichten gelangt. Später soll gezeigt werden, daß diese Auffassung die richtigere zu sein scheint. Hier sei darauf verwiesen, daß von den insgesamt fünf Proben, die einen kleinen Sauerstoffgehalt aufweisen, der durch biologische Aktivität bedingt ist, zwei einen extrem hohen Urangehalt zeigen.

In dem aus der Ostsee ausströmenden Wasser ist der Urangehalt nach unseren Messungen variabel. Diese Werte sind 0,7 und $1{,}13.10^{-6}$ g U/l. Sie liegen niedriger als der in der südlichen Ostsee gefundene Wert, der eine sogar niedriger als der in der nördlichen Ostsee gefundene. Man muß daraus folgern, daß das Wasser auf dem Weg zu und durch die Pforten der Ostsee einen Teil seines Urangehaltes verliert.

Verfolgt man nun das einströmende Wasser auf seinem Weg in der Ostsee, so nimmt der Urangehalt zur Bornholmtiefe etwas ab, um aber dann sprunghaft anzusteigen. Im Gebiet östlich und nördlich von Gotland findet man die höchsten Werte; westlich von Gotland hingegen ist der Wert schon wieder kleiner. Aber auch nördlich von Gotland in der Landsorttiefe wurde ein niedriger Uranwert mit $1{,}3.10^{-6}$ g U/l. gefunden. Der Salzgehalt des Wassers in der Gotland- und Landsorttiefe wie auch westlich von Gotland ist ungefähr derselbe (10,7 bis 13,7‰). Es können also auf dem Weg von der Gotlandtiefe Oberflächen- und Tiefenwasser höchstens zu gleichen Teilen gemischt worden sein, was aber nicht eine solche

Erniedrigung des Urangehaltes ergeben sollte, wie sie von uns festgestellt wurde.

Zur Bestimmung des Urangehaltes der Sedimente wurden an drei Punkten in sauerstoffarmen Tiefen Sedimentproben genommen. In der Richtung des einströmenden Wasser angeführt sind es folgende Tiefen: Gotlandtiefe, Landsorttiefe und südlich der Landsorttiefe. Der Oberflächenwert ist ungefähr 5.10^{-6} g U/g. Da Sedimente ganz allgemein 1 bis 2.10^{-6} g U/g. enthalten, ist damit der Nachweis erbracht, daß Uran im Sediment angereichert wurde. Sein Gehalt ist mit der Tiefe im Sediment veränderlich, was auf variable Anreicherung schließen läßt. Die kleinsten gefundenen Werte liegen etwas höher als 2.10^{-6} g U/g und damit in der Nähe des normalen Urangehaltes von Sedimenten. Der höchste Uranwert wurde in 8 bis 10 cm Tiefe des Sedimentes der Gotlandtiefe, die am nächsten der Uranananreicherung sowohl des Oberflächenwassers als auch des Tiefenwassers liegt, gefunden. Er erinnert mit seinem Betrag von 10.10^{-6} g U/g an die Werte, die von Strøm (1948) in den Faulschlämmen der norwegischen Fjorde gefunden wurden. Da man in der Ostsee mit einer durchschnittlichen Sedimentation von 0,5 bis 1 mm im Jahr rechnen kann, repräsentiert der ganze Bohrkern aus der Gotlandtiefe einen Zeitraum von ungefähr 260 bis 520 Jahren. Während dieser Zeit kann sich swohl die Sedimentationsgeschwindigkeit als auch die Intensität der Uranzufuhr geändert haben, was die Variationen mit der Sedimenttiefe erklären würde.

In der Ostsee liegt ein abgeschlossenes Wassersystem vor, über das man eine geochemische Bilanz aufstellen kann. Leider konnten wir nicht alle Zuflüsse untersuchen und sind daher gezwungen, aus der Verteilung des Urangehaltes in der Ostsee selbst auf den Urangehalt der von Süden einmündenden Flüsse zu schließen. Die Anzahl der Proben ist einerseits noch sehr klein und so können die hier gezogenen Schlüsse nur vorläufige sein. Auf der anderen Seite sprechen alle unsere Messungen dafür, daß Uran in der Ostsee ausgefällt wird. Die Abschätzung der totalen Ausfällung ist schwierig; wir glauben jedoch die Grenzen angeben zu können, in denen sie sich bewegen kann.

Die Uranzufuhr erfolgt durch die Flüsse und das durch den Belt und den Sund einströmende Meereswasser. Das letztere hat einen Urangehalt von $1{,}85.10^{-6}$ g U/l.; da das jährlich einfließende Volumen 737 km³ beträgt, werden insgesamt 1350 Tonnen Uran durch die Pforten der Ostsee transportiert. Dieses Wasser mischt sich aber schon zum größten Teil in der Beltsee mit dem ausfließenden Wasser. Infolgedessen erreicht nur ein kleiner Teil das Arkonabecken und die Gotlandsee. Wir rechnen aber doch mit dieser Menge, da unsere Proben an dieser Stelle genommen wurden; daher muß auch der Ausfluß hier berücksichtigt werden, der 1216 km³ jährlich beträgt. Die Uranwerte für diese Wassermasse schwanken zwischen 0,7 und $1{,}1.10^{-6}$ g U/l. Daraus folgt, daß zwischen 850 und 1350 Tonnen Uran aus der Ostsee transportiert werden. Der Ausfluß ist also *höchstens* so groß wie der Zufluß und im Mittel sollte ein Überschuß von Uran in der Ostsee verbleiben.

Nimmt man für die Flüsse einen Urangehalt von $0{,}5.10^{-6}$ U/l. an, so liefern die Flüsse im Bottnischen Meerbusen und im Finnischen Meerbusen mit einem jährlichen Transport von 330 km³ eine Uranzufuhr von 165 Tonnen. Der übrigen Flußzufuhr muß aber aus den oben angegebenen Gründen ein höherer Uranwert zugesprochen werden. Bei Zugrundelegung eines angenommenen Wertes von

3.10^{-6} g U/l. sollten diese Flüsse etwa 420 Tonnen Uran in die Ostsee einbringen. Die gesamte Zufuhr durch Flüsse würde also etwa 600 Tonnen Uran betragen.

Um eine Vorstellung über die Größenordnung des jährlich in den Sedimenten abgelagerten Urans zu erhalten, muß erst die Fläche der Sedimente und dann die Sedimentationsintensität abgeschätzt werden, um Rückschlüsse auf die totale Menge zu ermöglichen. Andererseits kann man jedoch auch von der durch die Flüsse transportierten Sedimentmenge ausgehen und die der Ostsee zugeführte totale Sedimentmenge berechnen. Beide Berechnungsarten führen auf 50 bis 100 Millionen Tonnen Sediment. Da in der Oberfläche des Sedimentes ein Urangehalt von etwa 5.10^{-6} g U/g gemessen wurde und der mittlere Gehalt der sedimentierten Minerale auf 2.10^{-6} g U/g geschätzt werden kann, werden der Ostsee an gelöstem Uran etwa 150 bis 300 Tonnen entnommen und in den Sedimenten angereichert. Aus dem erhaltenen Maximalwert von 10.10^{-6} g U/g würde sich eine maximale Ausfällung von 800 Tonnen Uran ergeben.

Aus einer Zusammentstellung der gewonnenen Resultate ergibt sich die Bilanz der Tabelle 6.

Tabelle 6.

Uran in Jahrestonnen		
Dem Ostseewasser zugeführt		aus der Ostsee entnommen
Flüsse:	600	0
Meerwasser:	1350	850 bis 1350
Sedimente:	0	150 bis 800
Total:	1950	1000 bis 2150

Damit die Bilanz nicht nur größenordnungsmäßig stimmt, ist die Annahme erforderlich, daß die aus der Ostsee abtransportierte Uranmenge ungefähr gleich groß der mit dem Meerwasser eingeführten ist und alles von den Flüssen zugeführte Uran in der Ostsee ausgefällt wird. Wie aber früher angeführt, ist die Bilanzberechnung eine sehr unsichere und die Ausfällung des Urans wird durch sie nicht bewiesen, sondern nur kontrolliert.

Für das geochemische Verhalten des Urans kann man das Redoxpotential in der Ostsee verantwortlich machen, da die vierwertige Form zur Komplexbildung mit organischen Substanzen neigt, während die Salze des sechswertigen Urans leichter löslich sind. Es sollte daher der Sauerstoffgehalt des Wassers die Verteilung des Urans beeinflussen. Es zeigt sich, daß beide korrelativ sind (Abb. 3), wenn auch die Verhältnisse nicht eindeutig sind, da die variable Zufuhr mit den Flüssen die Verhältnisse etwas verwischt. Die höchsten Uranwerte wurden in dem sauerstoffarmen Tiefenwasser gefunden; dagegen sind die Werte in der Oberflächenschicht durchwegs niedriger. Man kann sich den Prozeß der Ausfällung so vorstellen, daß das U(VI)-Ion durch organische Stoffe zum U(IV)-Ion reduziert und an organischem Detritus adsorbiert wird, wobei kolloidale Lösungen resultieren.

Dadurch wird das Uran dem Oberflächenwasser entzogen, sinkt langsam ab und reichert sich im Tiefenwasser an, wo es, da Sauerstoffmangel herrscht, nicht wieder in Lösung gebracht werden kann. Das Sauerstoffdefizit ist ebenso auf die biologische Aktivität zurückzuführen wie auch auf den langsamen Nachschub

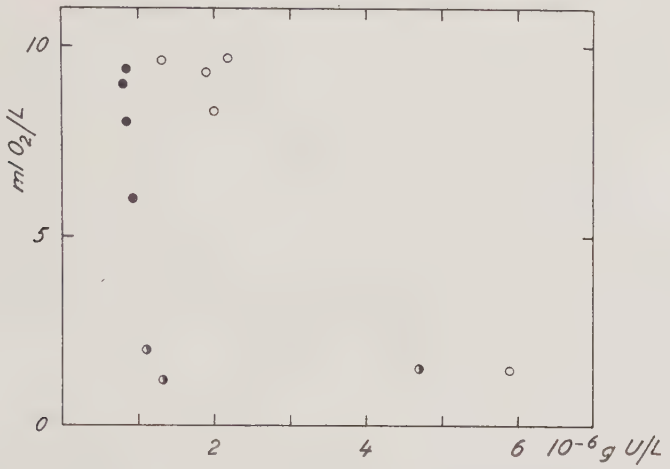

Abb. 3. Der Urangehalt der Meereswasserproben in Beziehung zum Sauerstoffgehalt. Leere Ringe kennzeichnen die hohen Werte der südlichen und östlichen Ostsee, halbvolle die Bodenwasserproben der westlichen Ostsee. Volle Ringe bezeichnen die Proben der nördlichen Ostsee.

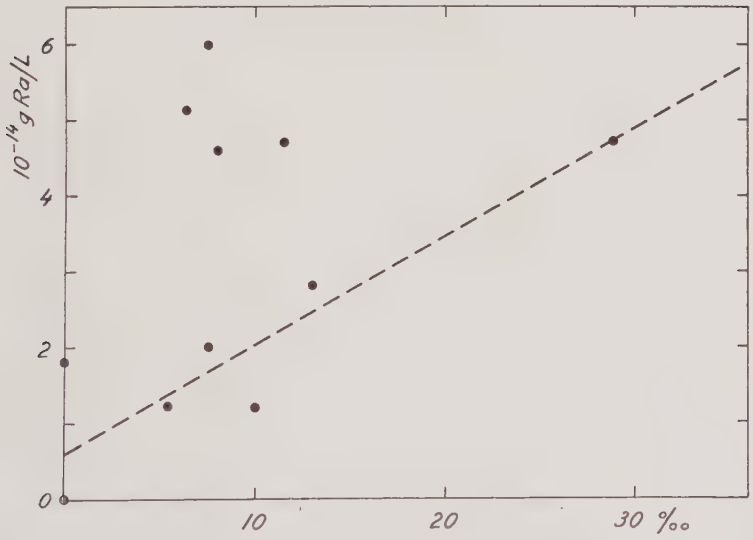

Abb. 4. Der Zusammenhang zwischen Salzgehalt und Radiumgehalt in den Wasserproben der Ostsee und zweier Flüsse.

von Wasser, das an der Oberfläche gewesen und dadurch mit Sauerstoff gesättigt worden ist. Damit scheint die Größe der Ausfällung des Urans am Meeresboden sowohl vom Austausch der Wassermassen als auch von der biologischen Aktivität abzuhängen, abgesehen von der Zufuhr durch Flüsse.

6. Der Radiumgehalt der untersuchten Wässer

Die Radiummessungen wurden vorgenommen, um eine Vorstellung über das radioaktive Gleichgewicht zu erhalten. Die Zahl der untersuchten Flüsse ist bis jetzt noch sehr klein und umfaßt hauptsächlich die Quellen, und da wieder solche, die für Heilzwecke verwendet werden. Dadurch dürfte der resultierende Mittelwert für den Radiumgehalt von Flüssen zu hoch sein.

Die zwei untersuchten Flußwässer, die beide aus dem Grundgebirge kommen, zeigen einen sehr kleinen Radiumgehalt. Bei dem einen Fluß (Indalsälv) fällt er sogar unter die Empfindlichkeitsgrenze der Apparatur. Leider waren keine Untersuchungsergebnisse aus Flüssen aus kalkreichen Gebieten verfügbar. Wie man aber aus dem Radiumgehalt der Ostsee folgern kann, scheinen diese Flüsse einen höheren Radiumgehalt aufzuweisen. Im Örekilsälv beträgt der Radiumgehalt nur 10% des auf Uran bezogenen Gleichgewichtswertes. Radium scheint also unter natürlichen Verhältnissen weniger ausgelaugt zu werden als Uran.

Der Radiumgehalt der Meeresproben zeigt ungefähr den gleichen Verlauf wie der Urangehalt, mit Ausnahme der Abhängigkeit vom Sauerstoffgehalt. Die östlichen Gebiete weisen einen höheren Radiumgehalt im Oberflächenwasser auf. Alle anderen Werte jedoch deuten auf einen Zusammenhang zwischen Salzgehalt und Radiumgehalt hin. Die extrapolierten Werte für Flußwasser und Ozeanwasser sind 1 bzw. 6.10^{-14} g Ra/l. (Abb. 4). Der so erhaltene Wert für Meerwasser mit 35‰ Salzgehalt entspricht dem Radiumgehalt, der in Nebenmeeren, wie dem Mittelmeer, dem Karibischen Meer und dem Roten Meer, in Proben der Schwedischen Tiefseeexpedition mit dem "Albatross", gemessen wurde (Koczy, 1956). Damit scheint auch die von Koczy vorgebrachte Theorie erhärtet, wonach der Radiumgehalt der Tiefsee, der bis zum Faktor 3 höher ist, vom ioniumreichen Tiefseesediment geliefert wird. Andererseits deutet der kleine Radiumgehalt des aus der Ostsee ausfließenden Wassers an, daß Radium irgendwo im Ostseeraum ausgefällt wird. Diese Ausfällung kann mit der Bildung von Kalkorganismen in Oberflächenschichten erfolgen. Da aber in der Ostsee alle Kalkschalen im kohlensäurereichen Wasser der Tiefen aufgelöst werden, sollte eine Anreicherung im Tiefenwasser gefunden werden. Als einzige Station, die dies vielleicht zu bestätigen vermag, können wir die Landsorttiefe anführen, wo das Tiefenwasser einen Gehalt von $4{,}7.10^{-14}$ g Ra/l. erreicht. Wirklich bindende Schlüsse auf die Geochemie des Radiums in der Hydrosphäre dürfen und sollen derzeit nicht auf unser noch so spärliches Material begründet werden. Es sei hier lediglich darauf hingewiesen, daß man nicht erwarten darf, es könnten sich in der Ostsee Gleichgewichtswerte zwischen Uran und Radium einstellen, da der Wasseraustausch gegenüber der Halbwertszeit des Radiums und insbesondere des Ioniums doch um Größenordnungen zu rasch vor sich geht.

7. Zusammenfassende Schlußfolgerungen

Die vorliegenden Untersuchungen zeigen, obwohl ihnen nur ein Teil der in die Ostsee einmündenden Flüsse zugrundelag, daß der Urantransport mit Flüssen sehr variabel ist. Es hat den Anschein, als ob Flüsse aus dem Grundgebirge im allgemeinen einen kleineren Urangehalt aufwiesen als Flüsse, die sedimentäres Gestein durchfließen. Dies kann mit der leichteren Löslichkeit, die das in Sediment

enthaltene Uran besitzt, zusammenhängen. Der Urangehalt des Flußwassers aus dem Grundgebirge ist im Mittel $0{,}5.10^{-6}$ g U/l. Dagegen muß angenommen werden, daß der Urangehalt der vom Süden und Südösten einmündenden Flüsse bis zu 10.10^{-6} erreicht, womit der hohe Urangehalt des Ostseewassers erklärt werden könnte.

Der Radiumgehalt der Flüsse steht nicht im radioaktiven Gleichgewicht mit dem Urangehalt, sondern beträgt nur etwa 10% des Gleichgewichtswertes. Daher darf man wohl voraussetzen, daß Uran im allgemeinen leicher ausgelaugt wird als Radium.

Die Verteilung des Urans im Wasser der Ostsee wird von der Verschiedenheit der Uranzufuhr durch Flußwasser, das salzreiche Wasser des Kattegatts, die Strömungen in der Ostsee und die biologische Aktivität bestimmt. Die Anreicherung des Urans in den sauerstoffarmen Schichten des Tiefenwassers ist wahrscheinlich durch kolloidale Ausfällung des Urans bedingt. Man kann annehmen, daß das Uran zur vierwertigen Form reduziert wird und mit organischen Zerfallsprodukten kolloidale, unlösliche Komplexe bildet, die sehr langsam sedimentieren. Sauerstoffarme Schichten können aber dann kein Uran anreichern, wenn die Zufuhr klein ist; andererseits erhielten wir Werte von ungefähr 5.10^{-6} g U/l. in den Tiefenwässern unter der durch Flußwasserzufuhr mit Uran angereicherten Oberflächenschicht. Abgesehen von diesen zwei Faktoren, Sauerstoffmangel und punktartig erhöhter Uranzufuhr, mischt sich der Urangehalt wie der Salzgehalt der Wässer. Die Anreicherung durch Sauerstoffmangel wurde auch im Ozeanwasser durch die Untersuchungen von G. Koczy (1950) festgestellt.

Die Ausfällung des Urans wurde durch Messungen an Sedimentproben erhärtet. Der Urangehalt der Sedimente, bedingt durch deren Gehalt an uranführenden Mineralen, wird um einen Betrag von 1 bis 8.10^{-6} g U/g gegenüber ihrem durchschnittlichen Gehalt erhöht. Die Schwankung der Uranausfällung kann durch Schwankungen sowohl der Zufuhr als auch der Ausbildung der sauerstoffarmen Schicht erklärt werden. Sollete es möglich sein, das kolloidale Uran gesondert zu bestimmen und eine Uranstratigraphie im Ostseegebiet zu begründen, die durch ^{14}C-Bestimmungen datiert werden könnte, so wäre damit auch die Möglichkeit gegeben, den Durchlüftungsgrad der Ostsee in geologischen Zeiten zu bestimmen.

Der Versuch, eine Bilanz für das Uran in der Ostsee aufzustellen, ist wegen der doch noch immer kleinen Zahl der Proben problematisch, scheint aber doch erörternswert. Man erhält dabei als Zufuhr durch Flußwasser etwa 500 bis 700 Tonnen Uran jährlich, durch das einströmende Meerwasser etwa 600 bis 700 Tonnen. Die mit Wasser abtransportierte Menge scheint zwischen 700 und 1000 Tonnen zu liegen. Dadurch ergeben sich als in der Ostsee selbst ausgefällte Uranmenge 100 bis 700 Tonnen jährlich. Setzt man plausible Werte für die Sedimentationsgeschwindigkeit und die Fläche ein, über der Uran ausgefällt wird, so erhält man die Uranbeträge, die tatsächlich im Sediment gefunden wurden.

Mit dieser Untersuchung wurde gezeigt, daß die vermutete Ausfällung von Uran am Schelf tatsächlich vor sich geht und daß deren Größenordnung gleich der der Zufuhr durch Flußwasser ist. Der Ausfällungsprozeß erfordert biologische Aktivität mit Erniedrigung des Sauerstoffgehaltes und eine gewisse Zeit. Uranführende Flüsse, die unmittelbar in den Ozean münden, wo solche Bedingungen

fehlen, können daher zu der Erhöhung des Urangehaltes im Weltmeere beitragen. Andererseits kann in Meeresbecken, die keine Uranzufuhr durch Flußwasser erhalten, das Uran des einströmenden Meerwassers ausgefällt ein Prozeß, der die uranreichen Ablagerungen des Dictyonemaschiefers erklärt, da in den berührten Meeresbecken die minerogene Sedimentation klein, die biogene aber groß war.

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Mesure des isotopes du thorium dans l'eau de mer

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(*Received* 19 *March* 1956)

Abstract—In order to study the geochemistry of thorium isotopes in the hydrosphere, particularly in the ocean, a method has been worked out by which Th-232 (thorium)λ, Th-230 (ionium), Th-228 (radiothorium), and Th-227 (radioactinium) can be determined separately. Eight samples of 20 to 40 litres of sea-water, from 23·0‰ to 34·97‰ salinity, were collected in November 1953, in the Skagerak and the Gullmarfjord (Sweden).

Thorium was isolated by the following procedure: just after collection, the samples were brought to pH 2 and a given amount of Th-234 (UX_1) was added as tracer. Thorium was first precipitated with $Fe(OH)_3$ as carrier. Further purification was obtained by ion-exchange column chromatography followed by solvent extraction; the final fraction was obtained as the citric complex, a form suitable to incorporation in the photographic emulsion. The total yield varied from 8 to 23% according to the sample, as determined by the β-activity of the tracer.

The various thorium isotopes were measured through their α-activity, using nuclear photographic emulsions, more precisely the double-emulsion technique. RdTh and RdAc both generate five-branched stars; more than 90% of these originated from RdTh, as indicated by the length of the tracks: while Io and Th only yield single tracks of range 18·8 μ and 15 μ respectively in the emulsion. Most samples showed a much lower activity than expected; this did not make it possible to discriminate between Io and Th through the range distribution of their tracks, thus we could only ascertain upper limits of Io and Th concentrations.

Average concentrations corresponding to a total volume of 140 litres of water are as follows (in grams per ml):

$$\text{RdTh} = (4{\cdot}0 \pm 1{\cdot}4) \,.\, 10^{-21} \qquad \text{Th} < 2 \,.\, 10^{-11}$$
$$\text{RdAc} < 7 \,.\, 10^{-23} \qquad \text{Io} < 6 \,.\, 10^{-16}$$

In one of these samples (salinity: 33·7‰) we have found an Io concentration of $26 \,.\, 10^{-16}$ g/ml. This high value is attributed to a nonhomogeneous distribution of Io in the sea.

Before the conclusions are drawn, we must point out the following restriction:

(1) Our water samples, including those in the oceanic range of salinity, were not collected in an oceanic environment, as all were taken in coastal waters.

(2) Our experimental results should correspond to the total thorium content of the samples. It must be pointed out, however, that a thorium fraction which both would not exchange with UX_1 at pH 2 and would not coprecipitate with $Fe(OH)_3$ would remain undetected with our procedure.

We assume the following concentration for the other radioactive elements: $U = 1{\cdot}5 \,.\, 10^{-9}$ g/ml, $Ra = 0{\cdot}8 \,.\, 10^{-16}$ g/ml, $Th \leqslant 6 \,.\, 10^{-12}$ g/ml.

The state of radioactive equilibrium between two nuclides A and B shall be defined by their activity ratio:

$$R_{A/B} = \frac{\lambda_A \,.\, N_A}{\lambda_B \,.\, N_B}$$

The following conclusions can be drawn from the above data:

(1) $R_{\text{Io/U-238}} < 0{\cdot}02$. More than 98% of the Io resulting from U-238 disintegration in the ocean cannot be accounted for. This lack of Io in the sea-water must be correlated with the presence of unsupported Io in the deep-sea sediments. These two corroborating facts definitely prove the hypothesis of ionium precipitation with the sediments.

(2) $R_{\text{Io/Ra}} < 0{\cdot}15$. Ra is in excess by a factor of 6 with respect to its equilibruim with Io. This could possibly result from the redissolution of part of the Ra originating from the Io of the sediments.

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(3) The average RdTh concentration of $4 \cdot 10^{-21}$ g/ml should correspond to an equilibrium concentration of $2{\cdot}6 \cdot 10^{-11}$ g/ml of the Th-232. We have, however, shown that, in at least two samples, RdTh is far over its equilibrium value with Th. Indeed, if we assume $Th < 6 \cdot 10^{-12}$ g/ml, this should lead to: $R_{RdTh/Th} > 4$. We can only account for this surprising result by supposing that the excess RdTh results from an excess of its parent $MsTh_1$ (Ra-228) brought in by rivers or redissolved from the sediments. Owing to the short half-life of both these nuclides, such a RdTh excess should be found only in the vicinity of the shore or the bottom.

(4) $R_{RdAc/U\text{-}235} < 0{\cdot}1$. More than 90% of the RdAc from U-235 in the ocean cannot be accounted for. Considering the short half-life of RdAc, this suggests that actinium or protactinium are precipitated with the sediments together with the Io.

(5) In both U-238 and Th-232 families, a radium isotope (Ra and MsTh) appears to be in excess over its parent thorium-isotope (Io and Th). The presence in the ocean of unsupported Ra($T = 1600$ years) and MsTh ($T = 6{\cdot}7$ years) is of great interest. A study of the distribution of these isotopes should yield valuable data on their diffusion rates and on deep currents.

As far as radioactive geochemistry is concerned, the ocean is characterized by extremely low concentrations of nuclides of all three radioactive families and by the total disruption of the radioactive equilibrium in these families.

A calculation of the geochemical balance of radioactive elements in the hydrosphere from the above data is given in the last part of the paper.

1. Introduction

Alors qu'il existe de nombreuses mesures valables de la concentration en uranium et en radium dans l'océan, il n'existe pas à notre connaissance de mesure directe du thorium et de l'ionium.

Le but de ce travail a été de développer une méthode de mesure de la concentration du thorium et de ses isotopes dans l'eau de mer et d'obtenir des résultats préliminaires sur ces concentrations.

Le comportement du thorium et de l'ionium dans l'océan présente un intérêt considérable pour la chronologie des sédiments océaniques et la balance géochimique des radio-éléments.

Le tableau 1 énumère les isotopes naturels du thorium avec leurs propriétés. Les isotopes présentant un intérêt géochimique sont soulignés.

Tableau 1. Isotopes naturels du thorium

Nom	Masse	Radioactivité	Période	Energie* en MeV
Th	232	α	$1{,}39 \cdot 10^{10} a.$	3,98
RdTh	228	α	$1{,}9\ a.$	5,42
UX_1	234	β	24,1 jλ.	0,20
Io	230	α	$8{,}0 \cdot 10^4 a.$	4,66
UY	231	β	24,6 h.	0,21
RdAc	227	α	18,6 j.	6,05

* Energie du groupe principal pour les α-Energie maximum du spectre β

L'Uranium dans l'océan

La concentration de l'uranium dans l'eau de mer a été mesurée par plusieurs auteurs, en général par fluorimétrie. Les premières mesures par Hernegger (1933) et Hernegger et Karlik (1935) sur les eaux côtières de la Suède ont donné des concentrations d'environ $1{,}1 \cdot 10^{-9}$ g U/ml. Gerda Koczy (1950) a trouvé

des valeurs très constantes autour de $1{,}3 \cdot 10^{-9}$ g U/ml dans les échantillons d'eau océanique prélevés par l'expédition de l'Albatross (1946–47); Smith et Grimaldi (1954) trouvent des valeurs comprises entre 1 et $3 \cdot 10^{-9}$ g/ml. Les déterminations de Nakamiski (1951) donnent des concentrations plus élevées de 2,5 à $3 \cdot 10^{-9}$ g/ml. Par contre Urry et Rona (1952) trouvent sur des échantillons d'eau océanique des valeurs systématiquement plus basses et présentant des écarts considérables d'un échantillon à l'autre. La validité de ces résultats a été discutée (G. Koczy, 1950, Pettersson, 1953) et les valeurs trop basses ont été attribuées à une adsorption de l'uranium sur les parois des récipients.

Enfin, Koczy, Hecht et Tomic (non publié), analysant les eaux de la mer Baltique de salinité beaucoup plus basse que l'eau océanique, trouvent des concentrations de 1 à $6 \cdot 10^{-9}$ g U/ml et dans les eaux de la Mer du Nord de 1,5 à $1{,}9 \cdot 10^{-9}$ g U/ml.

A part les valeurs de Urry et Rona, les résultats obtenus par fluorimétrie montrent une remarquable constance de la concentration en uranium, qui varie de 1 à $3 \cdot 10^{-9}$ g U/ml.

Les méthodes de mesure de l'Uranium par activation neutronique (Smales, 1952; Mahlman et Leddicotte, 1955), n'ont pas encore été appliquées à l'eau de mer. Une intéressante méthode développée par Stewart et Bentley (1954) et basée sur le comptage des fissions de U-235 a été appliquée par ces auteurs à des eaux côtières des Etats-Unis. La concentration moyenne en Uranium trouvée est de $2{,}5 \cdot 10^{-9}$ g/ml.

Le radium dans l'ocean a été mesuré la première fois par Joly (1908) puis par d'autres auteurs avec des résultats très erratiques.

Les premiers résultats vraiement dignes de confiance ont été obtenus indépendamment par deux groupes de chercheurs: Evans, Kip et Moberg (1938) trouvent des concentrations en Ra qui s'échelonnent entre 0,0 et $3{,}3 \cdot 10^{-16}$ g/ml. Les mesures de Pettersson et Rona (Föyn *et al.*, 1939) ont donné des valeurs très proches: de 0,2 à $2{,}9 \cdot 10^{-16}$ g Ra/ml.

Un grand nombre de déterminations de radium, encore non publiées ont été effectuées lors de l'expédition de l'Albatross. Les valeurs varient entre 0,3 et $1{,}8 \cdot 10^{-16}$ g Ra/ml avec une moyenne de $0{,}8 \cdot 10^{-16}$ g Ra/ml.

Ionium. Il n'y a pas, à notre connaissance, de mesure directe de l'ionium dans l'océan. Si on fait l'hypothèse que l'ionium est en équilibre avec le radium, on trouverait une concentration de l'ordre de $4 \cdot 10^{-15}$ g Io/ml. Holland et Kulp (1954), se basant sur des considérations très indirectes de balance géochimique, prévoient une concentrations de $3{,}1 \cdot 10^{-15}$ g Io/ml.

Thorium. Une mesure directe du thorium dans l'eau de mer a été tentée par Rona (Föyn, Karlik, Pettersson *et* Rona, 1939). Le thorium est coprécipité avec l'hydroxyde ferrique et mesuré par la méthode du thoron. Rona donne une limite supérieure de $5 \cdot 10^{-10}$ g Th/ml.

La valeur réelle est probablement beaucoup plus basse. Admettant l'hypothèse que la rapport thorium/ionium est le même dans l'océan et dans les sédiments pélagiques fraîchement déposés, Koczy (1949) calcule une concentration du thorium dans l'océan de 10^{-12} g Th/ml en se basant sur les valeurs moyennes connues des concentrations en radium dans l'océan et dans les sédiments et des

concentrations en thorium dans les sédiments. En effectuant ce calcul avec les valeurs du thorium et de l'ionium mesurées sur la même carotte (Picciotto et Wilgain, 1954), on trouve $6 \cdot 10^{-12}$ g Th/ml (Koczy, 1954).

L'hypothèse que l'ionium et le thorium sont précipités dans le même rapport parce qu'ils sont isotopes peut être inexacte si ces deux nuclides ne sont pas sous la même forme chimique. Il est probable qu'une partie seulement du thorium des sédiments provienne d'une précipitation chimique, le reste étant transporté à l'état de suspension. Dans ce cas, les valeurs calculées ci-dessus représentent une limite supérieure du thorium en solution vraie dans l'océan.

Non-equilibre radioactif et chronologie des sediments. Les mesures d'uranium et de radium dans l'eau de mer ont mis en évidence un fait capital de la géochimie des radioéléments dans l'océan: le défaut d'équilibre radioactif entre l'uranium et le radium. Si on admet une concentration en uranium de $2 \cdot 10^{-9}$ g/ml. la concentration du radium en équilibre serait de $3{,}4 \cdot 10^{-16}$ g Ra/ml, alors qu'on ne trouve que $0{,}8 \cdot 10^{-16}$. Ce défaut de radium dans l'océan correspond à l'excès bien connu de radium dans les sédiments océaniques (Joly, 1908; Pettersson, 1930.)

Pour expliquer cette situation Pettersson (1937) a émis l'hypothèse que l'ionium, parent direct du radium, est précipité au fur et à mesure de sa formation dans l'océan. Cette hypothèse a été confirmée par les nombreuses mesures de Piggot et Urry (1942) sur la distribution verticale du radium dans les carottes de sédiment.

La preuve directe de la présence d'ionium en excès, par rapport à l'équilibre avec l'uranium dans les sédiments océaniques a été apportée par les mesures d'ionium (Isaac et Picciotto, 1953) et d'uranium (Hahofer et Hecht, 1954) sur des carottes de l'expédition de l'Albatross.

Une conséquence très importante de ce comportement de l'ionium serait la possibilité de mesurer l'âge des sédiments océaniques jusqu'à environ 400.000 ans en arrière, en se basant sur la décroissance radioactive de l'ionium (période de 80.000 ans). Cette intéressante méthode a été proposée par Piggot et Urry (1942) et appliquée à de nombreuses carottes (Urry, 1942 à 1949).

L'interprétation des résultats est basée sur un certain nombre d'hypothèses que nous ne discuterons pas ici (voir Pettersson, 1953, Kröll, 1954).

Une méthode chronologique mettant un jeu moins d'hypothèses pourrait se baser sur la distribution dans le sédiment, non seulement de l'ionium, mais du rapport ionium-thorium (Picciotto et Wilgain, 1954). On a montré que cette méthode n'est valide que si le rapport ionium-thorium dans l'océan est le même que dans les sédiments actuels.

Un des buts du travail commencé ici est de rechercher si ce critère est vérifié.

Methodes de mesures de l'ionium et du thorium. D'après ce qui précède, on peut s'attendre aux concentrations suivantes pour l'ionium et le thorium dans l'eau de mer:

$$\text{Th} \leqslant 6 \cdot 10^{-12}\ \text{g/ml} = 7 \cdot 10^{-19}\ \text{curies}$$
$$\text{Io} \leqslant 4 \cdot 10^{-15}\ \text{g/ml} = 8 \cdot 10^{-17}\ \text{curies}$$

Ces valeurs expliquent que, malgré l'intérêt que présente ce problème, la concentration en thorium et ionium dans l'océan n'ait pas encore été mesurée. La

concentration en thorium dans les météorites métalliques, le matériel naturel le moins radioactif, est de l'ordre de 10^{-8} gr/gr.

La mesure de quantités absolues de 10^{-12} gr de thorium est impossible par les moyens connus. La concentration du thorium à partir de grands volumes d'eau pose des problèmes sérieux.

Les méthodes actuelles de mesure de traces de thorium peuvent se diviser en deux groupes:

(1) Les méthodes radioactives basées sur la mesure d'un descendant à vie courte.

La méthode classique par la mesure du Thoron permet de détecter 5 microgrammes de thorium. Pour mesurer le thorium dans les météorites, Dalton *et al.* (1953) ont utilisé l'activité α de ThB + ThC mesurée au compteur à scintillation ce qui permet de mesurer 10^{-6} gr de thorium. Deux méthodes radioactives plus sensibles (10^{-7} à 10^{-8} gr Th) ont été récemment développées à Bruxelles: une méthode photographique basée sur la formation d'étoiles dues aux désintégrations α successives à partir du RdTh (Picciotto et Wilgain, 1954) et une méthode électronique basée sur la distribution des intervalles de temps entre désintégrations α successives (Hirschberg, 1954). Ces méthodes mesurent en fait la concentration d'un des membres de la famille du thorium. Elles ne sont valables pour le thorium-232 que si ce dernier est en équilibre radioactif avec le descendant mesuré.

(2) Les méthodes mesurant directement le thorium.

La méthode colorimétrique de Kuznetsov (1944), développée par Thomason, Perry et Byerly (1949) permet le dosage de 10^{-6} gr de Th par cm^3. L'élégante méthode de dilution isotopique développée par Tilton, Aldrich et Inghram (1954) est une des plus sensibles (10^{-8} gr Th) mais nécessite un spectromètre de masse très perfectionné.

Une méthode basée sur l'activation neutronique du Th-232 a été récemment mise au point par Jenkins (1955).

Quant à l'ionium, une méthode permettant de mesurer des quantités de l'ordre de 10^{-11} g en présence d'autres isotopes du thorium a été décrite par Isaac et Picciotto (1953) pour le dosage de l'ionium dans les sédiments océaniques. Une méthode analogue a été suggérée par Baranov et Kuzmina (1954) mais en négligeant la présence des autres isotopes du thorium.

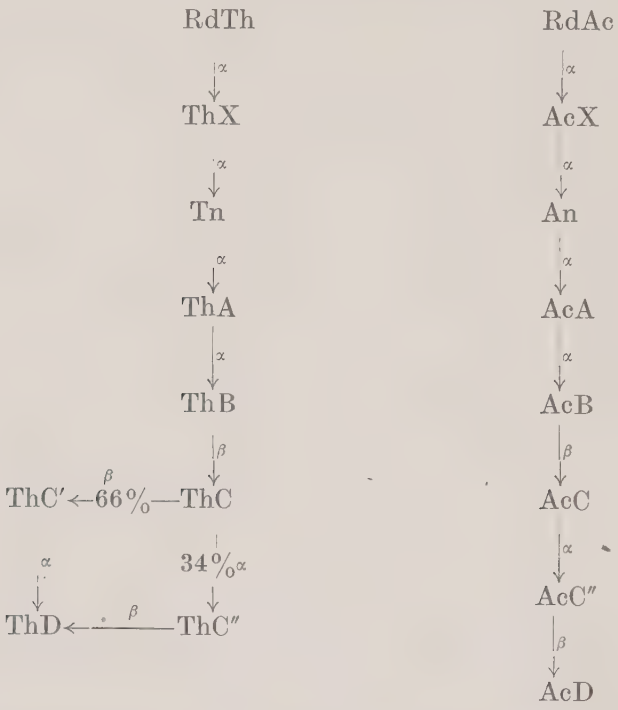
Methodes utilisées dans le présent travail

Nous avons utilisé la méthode appliquée aux sédiments océaniques. Nous en rappelons brièvement les principes. Elle sera discutée plus largement dans une autre publication. Les détails expérimentaux sont donnés au chapître suivant. Les radioisotopes α du thorium ont eté mésurés par la méthode des émulsions photographiques nucléaires (Powell, Chilton, Livesey, Occhialini, 1946) utilisant la technique de la double émulsion (Picciotto, 1949).

Des gouttes calibrées de la solution de Th sont déposées sur une couche d'émulsion, évaporées, puis recouvertes d'une seconde couche d'émulsion.

Cette technique permet de mesurer des activités de l'ordre d'un α par jour. Nous avons discriminé les divers isotopes d'apres leur présentation en traces simples ou en étoiles caractéristiques dues aux désintégrations successives. Les isotopes 230 (ionium) et 232 (thorium) ne donnent que des traces simples, les

isotopes 228 (RdTh) et 227 (RdAc) donnent des traces simples et des étoiles à 5 branches correspondant aux désintégrations successives suivantes:



Il est facile de montrer que dans la famille de l'uranium-238, la probabilité d'obtenir des étoiles à 5 branches est pratiquement nulle. Les désintégrations du radium donnent lieu à des étoiles à 4 branches.

La proportion d'étoiles formées pour les désintégrations du RdTh et du RdAc dépend du temps d'exposition. Cette fonction a été calculée par plusieurs auteurs. Le traitement mathématique le plus complet est donné par Flanagan et Senftle (1954). Pour un temps d'exposition de 30 jours, le pourcentage des désintégrations du RdTh et du RdAc formant des étoiles à 5 branches est respectivement de 82% et 52,5%. Les étoiles du RdTh sont distinguées de celles du RdAc par la présence de l'α du ThC′ dont le parcours dans l'émulsion est de 47 μ. Ce parcours beaucoup plus long que tous les autres, peut être caractérisé facilement, même dans de mauvaises conditions de mesure. A cause de l'embranchement du ThC, les 2/3 seulement des étoiles produites par le RdTh contiennent l'α du ThC′.

Des écarts expérimentaux au rapport théorique entre traces simples et étoiles peuvent être causés par la diffusion, dans l'émulsion photographique, des atomes et notamment des gaz rares isotopes du radon.

L'écart est considérable dans le cas du radium car la période de 3,5 jours du radon lui permet de migrer à une grande distance dans l'émulsion et même d'en sortir. Dans le cas du radiothorium, l'étoile à 5 branches peut être scindée en une

étoile à 2 branches (RdTh→ThX→) et une étoile à 3 branches (Tn→ThA→ThC), les deux étoiles restant généralement à une distance de quelques microns.

Dans un travail publié ailleurs (Picciotto et Wilgain), nous avons montré que la diffusion peut être complètement arrêtée en exposant à très basse température (Debeauvais-Wack, 1953) et que, en exposant à 4°C, la diffusion du thoron n'entraîne aucune erreur à condition de considérer la somme des étoiles à 5 branches et à deux branches. Dans le cas du radioactinium, la période de l'actinon (T = 3,9 sec) est trop courte pour que l'on puisse s'attendre à une migration appréciable.

La technique de la double émulsion permet de mesurer l'activité dans un volume de solution de l'ordre de quelques microlitres. Pour obtenir une activité spécifique élevée, il faut concentrer l'élément à doser dans le plus petit volume possible. Le problème chimique, dans notre cas, consiste à amener le thorium contenu dans 20 à 40 litres d'eau de mer dans un volume final de 0,1 cm³ au maximum.

Le thorium doit être purifié de tous les autres émetteurs α et doit être en solution sous une forme compatible avec son introduction dans l'émulsion photographique (Picciotto, 1949).

Aprés de nombreux essais en laboratoire, nous sommes arrivés au schéma de séparation suivant.

Vu le degré de purification requis, il est très difficile de récupérer le thorium quantitativement. L'expériénce nous a montré que le rendement est variable, même en essayant de garder toutes les conditions égales. Il est indispensable de mesurer le rendement des opérations chimiques au moyen d'un traceur radioactif. Le mieux adapté est le Th-234 (UX_1). Etant émetteur β, il n'interfère pas dans la mesure de l'activité α par la plaque photographique. Il est facile à mesurer et a une période maniable de 24 jours. Sa préparation est décrite au chapitre suivant.

Tous les échantillons d'eau ont été tracés par l'UX_1 dès leur prélèvement sur le bateau. La méthode n'est évidemment valable que si le thorium de l'eau de mer est échangeable avec le traceur. Ce point sera discuté dans la troisième partie du travail.

La première concentration du thorium a été effectuée par coprécipitation avec $Fe(OH)_3$ suivant la méthode utilisée par Rona (Föyn *et al.*, 1939).

Tous les autres cations, y compris les radio-éléments α: U, Ra et Po ont été éliminés par la suite des opérations décrites au chapitre suivant.

Le thorium a été finalement concentré dans un très petit volume de solution sous la forme de complexe citrique à pH 7.

Pour cette première expérience, nous n'avons pas eu la possibilité de prélever de l'eau réellement océanique. L'Office Suédois des Pêcheries a très aimablement mis à notre disposition son bateau de recherche "le Skagerak" et sa station hydrographique de Bornö, située dans le Gullmarfjord à 100 km au Nord de Göteborg et pourvu d'un excellent laboratoire.

Nous avons travaillé sur des échantillons d'eau du Skagerak d'une salinité très proche de la salinite océanique et sur des échantillons d'eau du Gullmarfjord.

2. Mesure des Isotopes du Thorium dans l'Eau du Skagerak et du Gullmarfjord

Les étapes de cette mesure sont les suivantes:

(1) Purification des réactifs et préparation de l'uranium X servant de radiotraceur.

(2) Prélèvements des échantillons, acidification et addition du traceur.

(3) Concentration du thorium par entraînement avec l'hydroxyde ferrique.

(4) Purification chimique du thorium.

(5) Mesure des isotopes du thorium par la méthode des émulsions nucléaires.

Les points 1,4 et 5 ont été traités à Bruxelles, 2 a été effectué à bord du bateua et 3 à la station de Bornö.

(1) *Purification des reactifs*

Un des problèmes majeurs est d'éviter la contamination des échantillons lors du traitement chimique. Nous pensons qu'il est utile de donner quelques détails sur les précautions prises qui nous ont permis de traiter 20 à 30 litres d'eau sans introduire plus de $2 \cdot 10^{-7}$ g de thorium et $2 \cdot 10^{-12}$ g d'ionium de contamination.

La procédure chimique a été choisie de façon à n'employer que des réactifs faciles à purifier. On a employé autant que possible des récipients en quartz ou en polyéthylène pour les opérations chimiques et la conservation des réactifs. Les opérations ont été effectuées à l'abri des poussières, notamment les évaporations.

Eau. L'eau distillée commerciale a été distillée deux fois dans un appareil entièrement en quartz et conservée dans des flacons en polyéthylène.

Acide chlorhydrique. De l'acide chlorhydrique environ 6 N correspondant au mélange azéotropique avec l'eau a été préparé par distillation d'HCl pur pour analyse dans un appareil entièrement en pyrex, et conservé dans des flacons en polyéthylène. L'acide plus concentré a été obtenu en équilibrant l'acide 6 N avec des vapeurs d'HCl en légère surpression par rapport à la pression atmosphérique.

Chlorure ferrique. $FeCl_3$ a été purifié par extraction à l'éther d'une solution de $FeCl_3$ en milieu HCl, 8 N dans un appareil à extraction continue. L'efficacité de cette purification a été vérifiée en ajoutant du Th-234 dans la solution de départ. Moins de 0,1% du Th-234 est passé dans l'éther avec $FeCl_3$.

Ammoniac. Toutes les précipitations d'hydroxyde ferrique ont été effectuées en faisant barboter de l'ammoniac gazeux à partir de bouteilles métalliques commerciales.

Acide nitrique. Purifié par distillation dans un appareil entièrement en pyrex.

Les autres produits tels que acide oxalique, acide citrique, chloroforme, sont des produits commerciaux purs pour analyse.

Préparation de l'uranium X. L'uranium X servant de traceur a été préparé à partir d'une solution de nitrate d'uranyle dans laquelle on a laissé recroître l'uranium X. Le plus grand soin doit être apporté à cette opération, la manipulation de solutions concentrées d'uranium présente un sérieux risque de contamination.

Un point très important est le contrôle de la concentration en ionium dans le traceur. Il est impossible d'éviter complètement la présence d'ionium qui croît à partir de U-234 pendant que l'uranium X croît à partir de U-238.

Le rapport de l'activité α de l'ionium à l'activité β de l'UX_1 est minimum pour un temps de recroissance infiniment petit; il vaut alors $8 \cdot 10^{-7}$.

Les variations de ce rapport en fonction des conditions d'extraction ont été calculées par Deutsch et Nikolic (1954). Nous avons utilisé la méthode de séparation de l'UX_1, décrite par ces auteurs, qui consiste à extraire le nitrate d'uranyle par l'éther, l'UX_1 restant dans la phase aqueuse. Une première extraction a été faite et la phase aqueuse contenant les isotopes

du thorium a été rejetée. On a remis le nitrate d'uranyle en solution aqueuse et on a laissé recroître l'UX_1 pendant 35 jours. Une seconde extraction de l'uranium a été effectuée. La solution d'UX_1 obtenue présentait alors les caracteristiques suivantes:

Rapport des activités α/β $= 1{,}3 \cdot 10^{-6}$
Activité β $= 1{,}06 \cdot 10^{3}$ désintégrations par cm^3 et par seconde
Concentration en ionium $= 1{,}93 \cdot 10^{-12}$ g/cm^3
Concentration en uranium $< 10^{-7}$ g/cm^3
(mesurée par fluorimétrie)

Au moment des mesures de l'Io de l'eau de mer, c'est-à-dire après un mois en moyenne, le rapport des activités α/β du traceur s'était élevé à une valeur proche de 10^{-5} pour les différentes analyses.

(2) *Prélèvement des échantillons d'eau*

Les échantillons d'eau ont été prélevés entre le 8 et le 21 novembre 1953. Les prélèvements ont été effectués à partir de la station hydrographique de Bornö située dans le Gullmarfjord, à 100 km au nord de Göteborg.

Les échantillons d'eau ont été prélevés avec une bouteille du type Nansen, en laiton nickelé, de 25 litres de capacité, qui avait servi pendant l'expédition de l'Albatross au prélèvement des échantillons pour les analyses de radium.

Les échantillons ont été immédiatement transvasés dans des récipients qui ont été, suivant les cas:

(a) des flacons en polyéthylène de 5 litres;

(b) des bouteilles en verre de 35 litres.

Le volume des échantillons a varié de 20 à 40 litres. Les récipients ont été préalablement rincés avec HCl purifié, puis avec quelques litres de l'eau à analyser.

Immédiatement après le transvasement, on a ajouté à chaque récipient un volume connu d'une solution contenant par litre: 11,6 g $FeCl_3$, $2{,}86 \cdot 10^{-8}$ curies d'UX_1, soit $1{,}06 \cdot 10^{3}$ désintegrations par seconde, 2,5 môles d'HCl.

Le volume ajouté était de l'ordre de 4 cm^3 par litre d'eau de mer, ce qui amenait le pH de l'eau à 2 environ. Les échantillons ont été agités pendant 15 minutes, puis équilibrés avec le traceur pendant 12 heures environ.

Les détails sur l'origine, le volume et la salinité des échantillons sont donnés au tableau 2.

(3) *Concentration du Thorium*

Douze heures après le prélèvement, on a effectué à Bornö une première concentration du thorium suivant la procédure utilisée par Rona: coprécipitation avec $Fe(OH)_3$.

L'hydroxyde ferrique est précipité en faisant barboter dans les récipients de l'ammoniac gazeux. Le précipité devient visible vers pH 6, l'opération est arrêtée à pH 9 pour éviter la précipitation massive de $Mg(OH)_2$. On laisse reposer $Fe(OH)_3$ pendant quelques heures, le liquide surnageant est d'abord siphoné, le précipité est ensuite centrifugé par fractions successives dans deux flacons en polyéthlène de 50 cm^3. Le volume final du précipité est environ 40 cm^3. Le récipient initial est rincé avec 100 cm^3 d'HCl purifié qui sont conservés dans un troisième

Tableau 2. Description des échantillons

No	Prise	Localisation	Date et heure du prélèvement	Profondeur du prélèvement	Fond à	Salinité	Température	Origine de l'eau
I	22,85 kg	Bornö	8/11/1953 10.00 h	15 m	50 m	23,0‰	10,7°	Courant baltique
II	22,70 kg	Skagerak 58° 14′ N 11° 11′ E	9/11/1953 14.00 h	75 m	95 m	33,70‰	12,37°	Mer du Nord
III	30,35 kg	Skagerak 58° 14′ N 11° 11′ E	9/11/1953 14.30 h	75 m	95 m	33,70‰	12,37°	Mer du Nord
IV	26,00 kg	Bornö	16/11/1953 16.00 h	18 m	33 m	32,2‰	11,85°	Skagerak
V	22,87 kg	Bornö	16/11/1953 16.00	18 m	33 m	32,2‰	11,85°	Skagerak
VI	30,16 kg	Skagerak 58° 15′ N 10° 51′ E	18/11/1953 7.45 h	120 m	150 m	34,97‰	—	Mer du Nord
VII	23,05 kg	Skagerak 58° 15′ N 10° 51′ E	18/11/1953 7.45 h	120 m	150 m	34,97‰	—	Mer du Nord
VIII	37,95 kg	Skagerak 58° 15′ N 10° 51′ E	18/11/1953 7.45 h	120 m	150 m	34,97‰	—	Mer du Nord

Tableau 3. Rendement de la coprécipitation avec $Fe(OH)_3$

No	Récipient utilisé	Rendement
I	verre	60%
II	verre	54%
III	polyéthylène	83%
IV	polyéthylène	74%
V	verre	76%
VI	polyéthylène	98%
VII	verre	93%
VIII	verre	88%

flacon en polyéthylène. Ces opérations peuvent être effectuées en 6 heures par une personne.

Les rendements de ces premières concentrations ont été mesurés par l'activité de l'UX_1; ils sont donnés au tableau 3.

Les rendements sont généralement voisins de 100%, mais sont variables et peuvent descendre jusqu'a 50% bien que nous ayons autant que possible maintenu les mêmes conditions.

L'échantillon VI a été tracé et acidifié comme les autres mais a subi une ultrafiltration sur un filtre en nitrocellulose à pores de 0,1 μ de diamètre maximum, avant de précipiter $Fe(OH)_3$. Près de 100% de l'UX_1 ont été récupérés par entraînement avec $Fe(OH)_3$. Ce rendement confirme que le thorium ajouté à l'eau de mer acidifiée à pH 2 reste en solution vraie et non à l'état colloïdal ou adsorbé sur les particules en suspension.

(4) *Purification du Thorium*

Le but de cette étape est:

(1) d'obtenir du thorium aussi pur que possible pour pouvoir réduire le volume final à 0,1 cm³ au maximum;

(2) d'éliminer tous les radio-éléments α autres que les isotopes du thorium.

On a suivi la même procédure que les sédiments océaniques (Isaac et Picciotto, 1953).

Les précipités de $Fe(OH)_3$ sont redissous dans HCl, et les solutions transvasées dans un bécher en quartz de 250 cm³, elles sont portées à l'ébullition, les particules insolubles qui étaient en suspension dans l'eau de mer sont séparées par centrifugation. On ajoute à la solution chlorhydrique 2 gr de NH_4Cl purifié pour éviter la précipitation de $Mg(OH)_2$ et on fait barboter NH_3 gazeux jusqu'à précipitation complète de $Fe(OH)_3$; le précipité est redissous dans 50 cm³ d'HCl 6 N, et on répète la précipitation par NH_3 en présence de NH_4Cl.

Extraction de $FeCl_3$ par l'éther. Le précipité de $Fe(OH)_3$ est dissous dans quelques cm³ de HCl, 11 N. L'acidité de la solution est mesurée par microtitration sur une petite fraction et ajustée par addition d'HCl, 11 N de façon à obtenir une solution 8 N. Cette solution est extraite par l'éther dans un appareil à extraction continue, jusqu'à disparition de la coloration due à $FeCl_3$. La solution est alors évaporée dans une capsule en quartz jusqu'à un volume de 5 cm³.

Extraction du polonium par la dithizone (Bouissières et Ferradini, 1950). Aux 5 cm³ de solution chlorydrique, on ajoute environ 50 cm³ d'eau pour amener le pH entre 0 et 1. La solution est extraite par 20 cm³ d'une solution contenant 1 gr de dithizone par 1000 gr de chloroforme. On effectue 4 extractions successives par 20 cm³, chaque extraction est suivie d'un lavage de la phase aqueuse avec du chloroforme pur.

Purification finale par échangeurs d'ions. La purification finale des autres cations, y compris le radium et l'uranium, est effectuée sur une colonne d'échangeur d'ions. On a utilisé l'amberlite IR-120, "reagent grade." La colonne de 15 cm de haut et 2 cm de diamètre est lavée avec de l'acide oxalique 0,5 M, de l'HCl, 5 M et de l'eau bidistillée. Le débit a été réglé à 0,3 cm³ par minute.

Après la dernière extraction à la dithizone, la solution est versée sur la colonne d'amberlite. On fait passer successivement 100 cm³ d'eau λ, 100 d'HCl 2,5 N, 100 d'HCl 5 N et 100 d'HCl 7 N. Comme les essais préliminaires l'ont montré, l'uranium, le radium et la presque totalité des cations étrangers sont élués, tandis que le thorium reste fixé quantitativement. La colonne est lavée par 250 cm³ d'eau et le thorium est élué par l'acide oxalique 0,5 N. L'élution est contrôlée par l'activité β de l'UX_1. Environ 250 cm³ d'acide oxalique sont nécessaires.

La solution oxalique est évaporée à 10 cm^3 dans une capsule de quartz, puis transférée par fractions successives dans un appareil à micro-distillation ou on chasse l'eau et l'acide oxalique. Le très faible résidu final est repris par 5 ml d'HCl 4 N chaud, la solution est évaporée à sec dans un micro-tube à essai en pyrex, de 1 cm^3 de volume.

Prèparation de la solution à déposer sur la plaque photographique. Le résidu sec est repris par 0,1 cm^3 de tampon acide citrique-citrate de sodium 0,1 M à pH 7. Le pH de la solution finale est contrôlé et, si nécessaire, réajusté à 7 par addition de NaOH 0,1 N avec une micro-pipette. Pour faire passer complètement le thorium en solution à l'état de complexe citrique, le tube contenant la solution est chauffé à plus de 100°C en autoclave, en atmosphère saturée de vapeur d'eau, ce qui évite l'évaporation du faible volume de liquide. S'il reste encore un résidu insoluble, on centrifuge le tube. La solution surnageante est aspirée dans une micro-seringue dont le piston est commandé par une vis micrométrique; après un dernier contrôle du pH, elle est prête à être déposée sur la plaque photographique sous forme de gouttes calibrées de $2 \cdot 10^{-3}$ cm^3.

Mesure du rendement. Le rendement total des opérations chimiques est mesuré par l'activité β de l'UX_1 sur une partie aliquote de la solution finale délivrée par la seringue. Cette opération est en même temps une calibration de la micro-seringue.

Les rendements chimiques totaux (pourcentage du thorium récupéré) sont donnés au Tableau 4. On voit qu'ils varient entre 10 et 20% sauf sur l'échantillon VI pour lequel 2% du thorium seulement a été retrouvé dans la fraction finale. Les pertes les plus importantes se sont produites à la dernière étape, lors de la reprise incomplète du résidu sec par le tampon citrate. Avant ce dernier stade, plus de 50% du thorium initial était encore présent.

Tableau 4. Rendements chimiques totaux

Echantillon	Rendement
I	8%
II	11%
III	12%
V	11%
VI	2%
VII	23%
VIII	8%
Blanc	18%

(5) *Mesure de l'activité α par la méthode photographique*

Dépôt des gouttes. Des gouttes de $2 \cdot 10^{-3}$ cm^3 de la solution citrique sont déposées avec la micro-seringue sur des plaques Ilford C-2 de 100 microns d'épaisseur. Les gouttes sont groupées par 2 sur des plaques de 5 × 2 cm. Elles sont séchées en présence de silicagel en 3 ou 4 heures. Sur l'emplacement visible des gouttes, on délivre à la pipette une goutte d'émulsion C-2 "in gel form", liquéfiée par chauffage à 45 C. Sur chaque plaque, on ajoute deux gouttes supplémentaires d'émulsion liquide qui serviront de témoin pour la détermination du background.

Les plaques sont séchées en présence de silicagel pendant 12 heures, à température ordinaire. Elles sont ensuite conservées à 4°C en atmosphère sèche jusqu'au moment du développement.

Pour chaque échantillon, on a préparé 50 gouttes pour lesquelles les temps d'exposition ont varié de 5 à 50 jours. L'absence de fading a été contrôlée par l'aspect des trajectoires et surtout par la constance de l'activité spécifique en fonction des temps d'exposition variables.

Développement. D'excellents développements ont été obtenus par la méthode à deux températures (Dilworth, Occhialini et Payne, 1948), utilisant un révélateur à l'amidol (Dilworth, Occhialini et Vermaesen, 1950), qui contient par litre d'eau distillée:

18 gr de sulfite de Na anhydre
35 gr d'acide borique
8 cm³ de KBr à 10%

Les conditions de développement sont les suivantes:

Imprégnation à 4°C pendant 1 h
Stade chaud à sec: 1 h à 18°C.

Le fixage et le lavage ont été effectués avec les précautions d'usage. Avant le séchage, les plaques ont été immergées dans un bain de glycérine (10 cm³ de glycérine + 90 cm³ d'eau) pendant 24 h pour empêcher la contraction de l'émulsion et augmenter ainsi la précision sur les mesures de longueur des traces (Mignone, 1951).

Observation microscopique. L'observation des trajectoires d'α a été effectuée au microscope binoculaire, à un grossissement de 500 fois (objectif à immersion). On a exploré tout le volume délimité par la double couche d'émulsion (environ 2 mm³). Toutes les particules α ont été comptées et classées suivant leur présentation en traces simples ou en étoiles à 2, 3, 4 ou 5 branches. On a soigneusement distingué les traces émises au sein de l'émulsion de celles qui ont une extrémité en contact avec le verre support ou avec la surface de l'émulsion.

Des contrôles ont été effectués en faisant observer les mêmes gouttes par différents microscopistes.

(6) *Calcul des concentrations et résultats*

Nous emploierons les symboles suivants:

α_x = nombre d'α attribués au nuclide x contenu dans l'échantillon.
N_α = nombre total d'α en traces simples.
α_T = nombre d'α de l'ionium associé à l'UX_1 ajouté comme traceur (calculé d'après Deutsch et Nikolic (1954).
E_5 = nombre d'étoiles à 5 branches.
B = nombre d'α dus au background de l'émulsion (mesuré sur les gouttes témoins).
t = temps d'exposition des émulsions photographiques en jours (nombre de jours écoulés depuis le dépôt des gouttes jusqu'au début du développement).
$E(t)_A$ = rapport du nombre d'étoiles à 5 branches provenant du nuclide A au nombre total des désintégrations de ce même nuclide. $E(t)$ pour RdAc et RdTh est donné par les courbes de la Fig. 1.
D_A = nombre total de désintégrations du nuclide A pendant le temps t.
P = volume de l'échantillon d'eau de mer en ml.
λ = constante radioactive en jour^{-1}.
M = masse atomique.
R = rendement des séparations chimique mesuré par la fraction de l'UX_1 récupéré.

La concentration de l'isotope du thorium de nombre de masse A est donnée en gr par ml par

$$C_A = \frac{D_A \cdot M}{6 \cdot 10^{23} \cdot \lambda \cdot P \cdot t \cdot R}$$

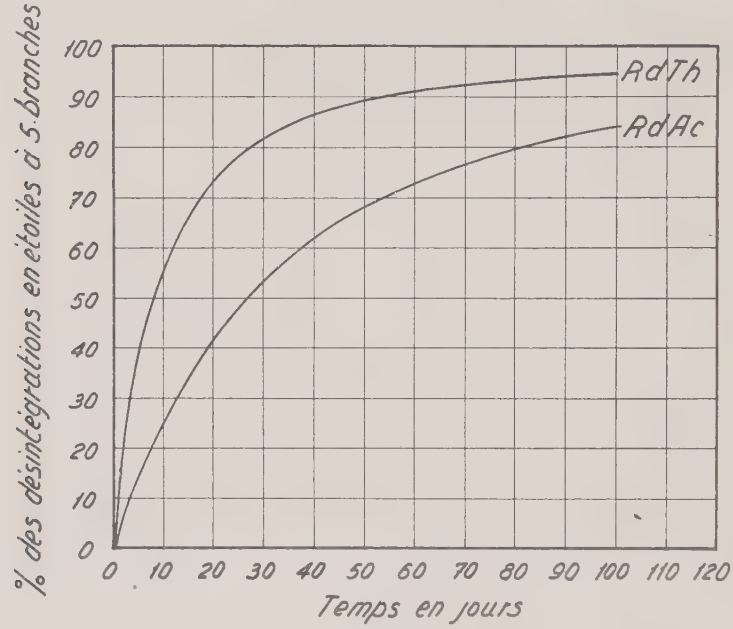


Fig. 1. $E(t)$: Fraction des désintégrations du radiothorium et du radioactinium se présentant en étoiles á 5 branches, en fonction du temps d'exposition

Calcul du Radiothorium (*Th*-228)

Toutes les étoiles à 5 branches (ainsi que les étoiles à 2 branches résultant de la migration du thoron) sont attribuées au radiothorium.

Le seul autre nuclide pouvant donner des étoiles à 5 branches est le radioactinium. En l'absence du RdAc, 66% des étoiles à 5 branches doivent contenir l'α du ThC′ caracterisé par sa longueur.

Le tableau 5 donne la proportion des étoiles contenant l'α du ThC′. On voit

Tableau 5. Proportion des étoiles à 5 branches contenant l'α du ThC'

Echant. No	Nombre total d'étoiles à 5 branches comptées	Nombre d'étoiles à 5 branches avec ThC'	Rapport expérimental $\frac{\text{Th}C'}{E_5}$
I	44	33	0,75 ± 0,25
II	70	51	0,64 ± 0,17
III	102	64	0,63 ± 0,13
V	76	50	0,66 ± 0,14
VII	163	104	0,64 ± 0,10
Rapport théorique			0,66

que pour tous les échantillons, l'écart du rapport théorique 0,66 est inférieur à l'erreur statistique moyenne. On peut en conclure que toutes les étoiles à 5 branches sont attribuables au RdTh dans les limites d'erreur expérimentale.

La concentration en gr de RdTh par ml d'eau est donnée par:

$$C_{228} = 3{,}79 \cdot 10^{-19} \cdot \frac{D_{228}}{P \cdot t \cdot R}$$

$$D_{228} = \frac{E_5}{E(t)_{228}}$$

Calcul du Radioactinium (Th-227)

Une limite supérieure de la concentration en radioactinium a été calculée en attribuant au RdAc un nombre d'étoiles à 5 branches correspondant à deux fois la déviation standard sur le rapport expérimental ThC'/E_5.

La concentration en RdAc est donnée par:

$$C_{227} = 1{,}01 \cdot 10^{-20} \cdot \frac{D_{227}}{P \cdot t \cdot R}$$

Calcul de l'Ionium et du Thorium (Th-230 *et* Th-232)

Les α en traces simples sont attribuables:
(1°) au Th-232 (100% des désintégrations en traces simples).
(2°) à l'ionium (100% des désintégrations en traces simples).
(3°) au RdTh, la fraction des désintégrations en traces simples est égale à

$$\frac{(1 - E(t))E_5}{E(t)}$$

En dehors de la contamination apportée par les réactifs, les corrections suivantes doivent être apportées:

(1°) activité α due à l'ionium contenu dans la solution d'UX_1.
(2°) activité α due à la contamination radioactive de l'émulsion photographique.

La correction due à l'ionium contenu dans l'UX_1 a été calculée, suivant Deutsch et Nikolic (1954). Le background α de l'émulsion a été déterminé sur les gouttes témoins d'émulsion.

Il nous est impossible de discriminer les traces simples dues au Th-232 et à l'ionium. Vu le faible nombre total d'α et la contribution du RdTh et du background, la distribution des longueurs ne donne pas de résultat clairement interprétable sauf dans le cas de l'échantillon II (Fig. 2).

Il y trois cas pour lesquels il est possible de calculer les concentrations en Io et Th:

(a) Th-232 et RdTh sont en équilibre radioactif.

Le nombre d'α dus au Th-232 est égal au nombre de désintégrations du RdTh.

$$D_{232} = \alpha_{\mathrm{Th}} = D_{228}$$

$$D_{230} = \alpha_{\mathrm{Io}} = N_\alpha - (\alpha_{\mathrm{RdTh}} + \alpha_T + B + D_{228})$$

(b) La concentration en ionium est nulle

Dans ce cas,

$$\alpha_{\mathrm{Io}} = 0$$
$$\alpha_{\mathrm{Th}} = N_\alpha - (\alpha_{\mathrm{RdTh}} + \alpha_T + B)$$

Si l'équilibre n'est pas établi, on peut seulement donner une limite supérieure pour le Th-232 en lui attribuant tous les α simples, ce qui revient à supposer que la concentration en Io est nulle.

(c) La concentration en Th-232 est nulle

$$\alpha_{\mathrm{Th}} = 0$$
$$\alpha_{\mathrm{Io}} = N_\alpha - (\alpha_{\mathrm{RdTh}} + \alpha_T + B)$$

On peut donner une limite supérieure pour la concentration en ionium en attribuant tous les α à l'Io et en supposant que la concentration en Th-232 est nulle.

Nous démontrerons plus loin que dans certains échantillons, RdTh et Th ne sont pas en équilibre radioactif.

Les concentrations en Th et en Io sont données respectivement par:

$$C_{232} = 2{,}83 \cdot 10^{-9} \cdot \frac{D_{232}}{P \cdot t \cdot R}$$

$$C_{230} = 1{,}61 \cdot 10^{-14} \cdot \frac{D_{230}}{P \cdot t \cdot R}$$

A titre d'exemple, nous donnons les résultats expérimentaux et les calculs détaillés pour les échantillons no. II et VII dans les tableaux 6 et 7.

Tableau 6. Détail des résultats sur l'échantillon II (6 gouttes observeés)

t en jours	N_α	$\frac{N_\alpha - B}{t}$	E_5	$E_{(t)}$	D_{228}/t
17,9	184	9,7	6	0,69	0,5
17,9	172	9,0	7	0,69	0,6
27,7	278	9,6	12	0,79	0,5
38,8	351	8,7	23	0,85	0,69
42,8	—	—	25	0,87	0,68
42,8	318	7,1	23	0,87	0,66
98,0	867	8,6	65	0,92	0,72

N_α total $= 2170$ $\qquad R = 1{,}30\%$

$\alpha_{\mathrm{RdTh}} = 32{,}8$

$\alpha_T = 6{,}6$

$B = 82{,}4$

$D_{228} = 160{,}2$

Si on admet que RdTh et Th-232 sont en équilibre

$$\alpha_{\mathrm{Io}} = 1888$$

et $$C_{230} = (25{,}2 \pm 0{,}5) \cdot 10^{-15}\ \mathrm{g/ml}$$

Les longueurs des α simples ont été mesurées. Leur distribution est représentée à la Fig. 2 et démontre que la grande majorité des α simples sont dus à l'ionium.

Tableau 7. Détail des résultats sur l'échantillon VII (10 gouttes observées)

t en jours	N	$\frac{N_\alpha - B}{t}$	E_5	$E(t)$	D_{228}/t
13,8	20	1,1	8	0,60	1,0
13,8	13	0,6	6	0,60	0,7
15,9	26	1,3	9	0,65	0,9
36,8	52	1,2	24	0,84	0,77
36,8	32	0,7	24	0,84	0,77
57,8	51	0,7	37	0,90	0,72
57,8	41	0,5	29	0,90	0,55
81,8	74	0,7	43	0,92	0,42
81,8	95	1,0	68	0,92	0,67
90,8	121	1,1	71	0,92	0,65

N_α total = 525 $\quad \alpha_T = 229 \quad R = 4{,}69\%$

$\alpha_{\text{RdTh}} = 46 \quad D_{228} = 366$

$B = 95$

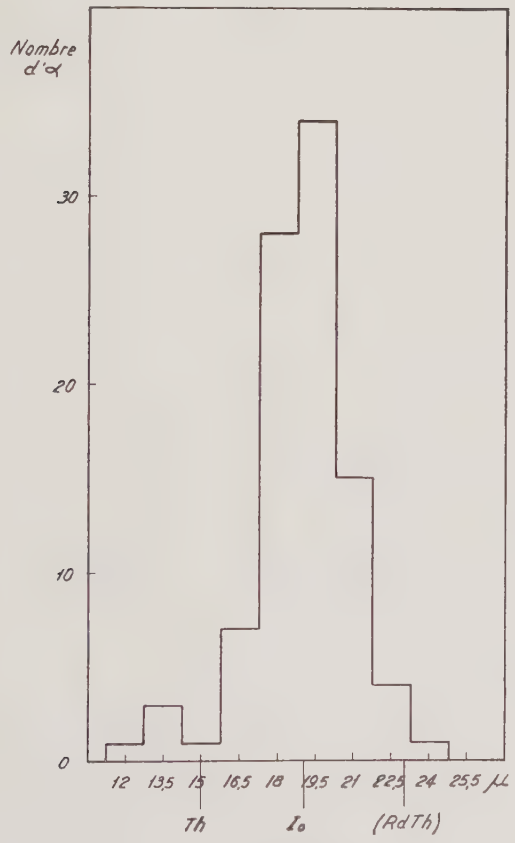


Fig. 2. Distribution des parcours des α dans la fraction finale de l'échantillon II.

Si on suppose que Th et RdTh sont en équilibre, on obtient: $\alpha_{Io} = -211 \pm 35$ soit un nombre d'α négatif, l'écart à zéro étant égal à six fois la déviation standard sur le nombre d'α comptés.

La seule interprétation de ce résultat est que le RdTh est fortement en excès par rapport à l'équilibre avec Th-232.

On peut obtenir une limite supérieure pour la concentration en ionium en supposant $C_{232} = 0$; dans ce cas, $\alpha_{Io} = 155$ et $C_{230} = 0{,}5 \cdot 10^{-15}$ g/ml.

Le tableau 8 donne pour chaque échantillon, les résultats expérimentaux des mesures d'activité α. Les erreurs indiquées représentent la deviation standard sur le nombre de désintégrations.

Soulignons que dans les échantillons VII et VIII, le radiothorium est certainement en excès par rapport à l'équilibre avec le thorium car, même si on suppose que la concentration en ionium est nulle, il n'y a pas assez d'α simples pour équilibrer le nombre d'étoiles à 5 branches. Si on suppose l'équilibre établi, on arrive à un nombre d'α simples négatifs. Ce même effet s'observe dans les échantillons III et V, mais il reste dans les limites des fluctuations statistiques. Le manque d'équilibre radioactif dans VII et VIII a pu être mis en évidence grâce à la très faible concentration en ionium. Dans les autres échantillons, on ne peut rien conclure sur l'état d'équilibre entre Th et RdTh à cause de l'excès de traces simples dues à l'ionium.

Les rendements R figurant au tableau 8 représentent la fraction du thorium total contenue dans la partie aliquote ayant servi à la mesure de l'activité α.

Tableau 8. Résultat des mesures d'activité

No. éch.	α simples	α_{RdTh}	α_T	B	D_{RdTh}	D_{Io} (équilibre (Th—RdTh)	$D_{Io\,max}$ (Th = 0)	R (en%)
I	421	18	8	108	97 ± 10	190 ± 15	287 ± 15	1,26
II	2.170	33	7	82	160 ± 13	1.888 ± 41	2.048 ± 41	1,30
III	402	58	15	48	299 ± 19	−20 ± 30	280 ± 30	2,35
V	304	40	8	48	213 ± 17	−5 ± 25	208 ± 25	1,98
VI	238	4	1	40	21 ± 4	171 ± 17	192 ± 17	0,21
VII	525	46	229	95	366 ± 19	−211 ± 35	155 ± 35	4,69
VIII	558	49	140	115	349 ± 18	−95 ± 34	254 ± 34	2,08
Blanc	778	16	206	140	130 ± 11	286 ± 35	416 ± 35	5,04

Le restant (par rapport aux rendements totaux du tableau 4) a servi à la mesure de l'activité β de l'UX_1.

Le tableau 9 donne les concentrations en RdTh, Th, Io et RdAc calculées suivant la manière décrite plus haut.

La signification des diverses colonnes est la suivante:

RdTh: concentration en radiothorium calculée d'après le nombre d'étoiles à 5 branches (qui sont toutes attribuables au RdTh). C'est une donnée expérimentale directe.

Th équivalent: concentration du thorium-232 qui serait en équilibre radioactif avec le RdTh.

Th maximum: limite supériéure de la concentration en thorium-232, obtenue en supposant la concentration en ionium nulle et en attribuant tous les α simples au Th-232.

Tableau 9. Concentrations des isotopes du thorium

No. éch.	RdTh	Th équivalent (équilibre Th-RdTh)	Th max. (Io = 0)	Io (équilibre Th-RdTh)	Io max. (Th = 0)	RdAc max.
	10^{-21} g/ml	10^{-11} g/ml	10^{-11} g/ml	10^{-16} g/ml	10^{-16} g/ml	10^{-23} g/ml
I	3,8 ± 0,4	2,8 ± 0,3	8,5 ± 0,4	3,2 ± 0,3	4,8 ± 0,3	9
II	5,1 ± 0,4	3,8 ± 0,3		25,2 ± 0,5	27,8 ± 0,6	9
III	6,1 ± 0,5	5,5 ± 0,5	4,2 ± 0,5	−0,2 ± 0,3	2,4 ± 0,2	9
V	5,5 ± 0,5	4,1 ± 0,4	3,6 ± 0,4	−0,1 ± 0,3	2,3 ± 0,3	8
VII	2,3 ± 0,1	1,7 ± 0,1	0,8 ± 0,2	< 0	0,5 ± 0,1	3
VIII	4,4 ± 0,2	2,9 ± 0,1	2,2 ± 0,3	< 0	1,2 ± 0,1	6
Blanc	0,8 ± 0,1	0,6 ± 0,1	2,0 ± 0,2	0,7 ± 0,1	1,0 ± 0,1	1

Io: concentration en ionium calculée avec l'hypothèse que Th et RdTh sont en équilibre.

Io maximum: limite supérieure de la concentration en ionium, obtenue en supposant la concentration en thorium nulle et en attribuant tous les α simples à l'ionium.

RdAc maximum: limite supérieure de la concentration en radioactinium calculée d'après le nombre maximum d'étoiles à 5 branches attribuables au RdAc.

On trouvera dans le tableau 10 les concentrations moyennes calculées sur les 5 échantillons d'eau à haute salinité représentant un volume total de 140 litres (éch. no. II, III, V, VII et VIII). L'échantillon I a été exclu de la moyenne, vu sa très basse salinité. On a soustrait l'effet dû à la contamination des réactifs.

Tableau 10. Concentrations moyennes en grammes par ml

Radiothorium	(Th-228)	$(4{,}0 \pm 1{,}4)^* \cdot 10^{-21}$
Thorium	(Th-232)	$< 2 \cdot 10^{-11}$
Ionium	(Th-230)	$< 6 \cdot 10^{-16}$
Radioactinium	(Th-227)	$< 7 \cdot 10^{-23}$

* Ecart quadratique moyen sur les 5 mesures

(7) *Discussion des résultats*

Avant de tirer des conclusions des résultats du tableau 9 deux remarques s'imposent:

(1°) *Sur la valeur des échantillons.* Une restriction importante à nos conclusions est que nos échantillons sont loin d'avoir été prélevés dans un environnement réellement océanique. Trois d'entre eux (VI, VII et VIII) ont une salinité très proche de la salinité océanique, mais ont été prélevés très près de la côte et du fond. Il est difficile de prévoir les effets de ces conditions de prélèvement. On peut aussi bien attendre des valeurs trop hautes des concentrations en éléments radioactifs à cause de la contamination par des posssières en suspension, surtout au voisinage d'une côte granitique, comme on peut supposer qu'une partie des radioéléments en solution a été adsorbée par les sédiments avec lesquels la masse d'eau est restée longtemps en contact.

(2) *Sur la signification des concentrations mesurées.* La solubilité expérimentale d'un cation comme le thorium n'a pas de signification thermodynamique définie, comme l'ont mis en évidence les travaux sur les "radiocolloïdes."* Pour ces cations lourds et fortement hydrolysables dans un milieu tel que l'eau de mer à pH 8, on peut s'attendre à trouver tous les états intermédiaires entre le cation simple en vraie solution ionique et l'aggrégat colloïdal. Aussi est-il important de définir clairement la signification de la concentration que l'on mesure, ce qui est souvent difficile dans le cas d'éléments en traces dans l'eau de mer.

D'après les conditions de mesure décrites plus haut, nos concentrations des isotopes du thorium représentent la somme de:

(a) les isotopes du thorium présents sous une forme échangeable avec l'UX_1, dans une solution d'eau de mer acidifiée à pH 2, après un temps d'équilibration de 12 heures, et

(b) les isotopes du thorium entraînés par le précipité de $Fe(OH)_3$ et redissous dans HCl 6 N à l'ébullition.

Il semble raisonnable d'admettre que la somme de ces deux termes représente le *thorium total* présent dans notre échantillon. Seuls auraient pu échapper à notre mesure les atomes de thorium non échangeables à pH 2 et non entraînables par $Fe(OH)_3$ à pH 9, par exemple le thorium engagé dans des complexes non dissociables, solubles et stables de pH 2 à pH 9.

Concentration en radiothorium et thorium. La concentration en radiothorium est relativement constante dans tous les échantillons; elle est de l'ordre de $4 \cdot 10^{-21}$ g/ml, soit un effet d'un facteur 5 par rapport à la contamination des réactifs.

Cette concentration serait en équilibre radioactif avec une concentration en *thorium* de $2{,}6 \cdot 10^{-11}$ g/ml.

La *limite supérieure* de la concentration en thorium calculée d'après les α simples est très voisine, elle est de $2 \cdot 10^{-11}$ g/ml. Cette limite est compatible et pas très éloignée de la valeur attendue de $6 \cdot 10^{-12}$ (voir Introduction).

Etat de l'equilibre radioactif dans la famille du Th-232. Dans deux échantillons au moins (VII et VIII), le RdTh est en excès par rapport à l'équilibre avec le Th. Il est probable par analogie, que cette situation existe aussi dans les autres échantillons, mais nous ne pouvons pas le prouver.

* voir, par exemple, l'ouvrage classique de Haïssinsky: *Les radiocolloïdes* Hermann, Paris (1934).

Nous exprimons l'état de l'équilibre radioactif entre deux nuclides A et B de la même famille par le rapport des activités $R_{A/B} = \frac{\lambda_A N_A}{\lambda_B N_B}$ qui est évidemment égal à l'unité lorsque l'équilibre est établi et respectivement plus petit ou plus grand que 1 lorsque A est en défaut ou en excès par rapport à B.

Si nous admettons pour la concentration limite en thorium, la valeur de $6 \cdot 10^{-12}$ g/ml, on a $R_{\mathrm{RdTh/Th}} \geqslant 4$.

Ce manque d'équilibre entre Th et RdTh est au premier abord surprenant étant donné que Th et RdTh, non seulement appartiennent à la même famille mais sont encore isotopes.

La seule explication que nous puissions proposer est que le RdTh en excès est soutenu par son parent, le mésothorium 1 (Ra-228). Celui-ci étant un radium est a priori plus stable en solution que le thorium et a pu se concentrer dans l'eau des rivières et de l'océan. Ce point est discuté dans le dernier chapitre. Une preuve de cette hypothèse serait donnée par une mesure directe du MsTh dans l'eau de mer, ce qui serait avec les moyens actuels, une entreprise difficile.

Concentration en ionium. Pour tous les échantillons, sauf le no. II, la concentration en ionium est de l'ordre de 10^{-16} g/ml.

L'échantillon no. II montre des valeurs en ionium 20 fois plus élevées. Cette discordance est difficile à expliquer, car les no. II et III font partie de la même masse d'eau.

Malgré la valeur de l'essai à blanc, on pourrait avancer l'hypothèse d'une contamination radioactive. La distribution des longueurs des α (Fig. 2) démontre que l'activité α mesurée est bien due à l'ionium. La concentration en RdTh ne montre pas d'accroissement par rapport aux autres échantillons. Il est improbable qu'une contamination accidentelle ait apporté un excès d'ionium sans être accompagnée de Th et RdTh.

Si on rejette l'hypothèse de la contamination, il faut admettre que l'accroissement de l'ionium dans l'échantillon II est dû à une distribution non homogène dans l'eau de mer, par exemple à l'existence d'agrégats colloïdaux.

La quantité totale d'ionium contenue dans les 20 litres de l'échantillon II se monte à $0{,}6 \cdot 10^{-10}$ g, soit $2 \cdot 10^{11}$ atomes. Vu la forte fluctuation par rapport aux autres résultats, il est probable que cette quantité totale est distribuée sur un très petit nombre de particules colloïdales. Dans ce cas, les dimensions linéaires de ces particules d'ionium seraient de l'ordre du micron.

Une autre explication de l'excès d'ionium dans l'échantillon no. II serait la présence d'un fragment d'un minéral riche en uranium, mais ne contenant pas de thorium, en suspension dans l'eau. La quantité d'ionium présente équivaut à $3 \cdot 10^{-6}$ g d'uranium. En supposant une teneur en uranium de 50% et une densité de 5 pour ce minéral, le fragment responsable aurait des dimensions de l'ordre de 100 microns.

Même en incluant l'échantillon no. II dans les résultats, on trouve que la concentration moyenne en ionium est inférieure à $6 \cdot 10^{-16}$ g/ml. Cette limite supérieure est 10 fois plus faible que la concentration attendue sur la base des considérations développées dans l'Introduction. Ceci explique la faible précision de nos mesures et la valeur relativement haute des activités α dues à la contamination

des réactifs et à l'UX_1, car nous ne nous étions pas préparés à mesurer des concentrations si faibles.

Etat de l'equilibre radioactif dans la famille de U-238. Nous admettrons que la concentration moyenne en uranium est de $1{,}5 \cdot 10^{-9}$ g/ml et la concentration en radium de $0{,}8 \cdot 10^{-16}$ g/ml. L'uranium a été mesuré par fluorimétrie sur des parties aliquotes de nos échantillons IV et VIII par le Dr. Hecht qui a bien voulu nous communiquer les résultats suivants, qui seront repris dans une autre publication:

Ech. IV : $1{,}4 \cdot 10^{-9}$ g U/ml (non filtré)

id. : $1{,}7 \cdot 10^{-9}$ g U/ml (filtré)

Ech. VIII : $1{,}2 \cdot 10^{-9}$ g U/ml (non filtré)

La quantité d'ionium en équilibre avec $1{,}5 \cdot 10^{-9}$ g d'uranium est $2{,}5 \cdot 10^{-14}$ g alors, qu'en moyenne, nous trouvons moins que $6 \cdot 10^{-16}$ g et, dans la majorité des échantillons, moins que 10^{-16} g. On a donc:

$$R_{\mathrm{Io/U}} < 0{,}02$$

Plus des 98% *de l'ionium produit par l'uranium-*238 *dissous dans l'océan sont absents dans l'eau de mer.* Ce défaut d'ionium dans l'océan correspond à son excès dans les sédiments. Ces deux évidence complémentaires apportent la preuve directe de l'hypothèse de précipitation de l'ionium avec les sédiments, avancée par H. Pettersson et confirmée par les mesures d'uranium et de radium dans les sédiments et dans l'eau de mer.

D'après nos résultats, l'ionium est *totalement* précipité (à 1 ou 2% près) alors qu'en se basant sur les concentrations en radium, on prévoyait une précipitation de 80 à 85%.

Une conséquence inattendue de ces résultats est que Ionium et Radium ne sont pas en équilibre. En effet, si on prend $U = 1{,}5 \cdot 10^{-9}$ g/ml et $Ra = 0{,}8 \cdot 10^{-16}$ g/ml, on a:

$$R_{\mathrm{Ra/U}} = 0{,}16$$

et

$$R_{\mathrm{Io/Ra}} < 0{,}15$$

Le radium est en excès d'un facteur 6 environ par rapport à l'équilibre avec l'ionium.

Cette situation pourrait être purement locale et due au caractère non océanique de nos échantillons. Elle pourrait aussi signifier que la concentration moyenne admise pour le radium est trop haute.

Que cette situation soit réelle et générale ne pourra être prouvé que par des mesures supplémentaires d'ionium et de radium sur des échantillons d'eau réellement océanique. Elle pourrait alors seulement s'expliquer comme on le verra plus loin par une redissolution du radium formé dans les sédiments à partir de l'ionium précipité. Une telle explication est compatible avec les propriétés chimiques respectives du radium et du thorium.

Pour terminer, il est interéssant de souligner le parallélisme de la situation dans les familles de Th-232 et U-238: dans les deux familles, un isotope du radium

(Ra et $MsTh_1$) semble être en excès par rapport à l'isotope du thorium dont il est le descendant (Io et Th). Les applications possibles à l'océanographie seront discutées plus loin.

Concentration en radioactinium et équilibre dans la famille de U-235.

La *limite supérieure* de la concentration en radioactinium est de $7 \cdot 10^{-23}$ g/ml.

Si on admet une concentration en uranium total de $1{,}5 \cdot 10^{-9}$ g/ml, on aura une concentration en U-235 de $1{,}15 \cdot 10^{-11}$ g/ml qui serait en équilibre avec $8 \cdot 10^{-22}$ g de RdAc.

On en conclut que 90% du radioactinium produit par U-235 sont absents et que

$$R_{\text{RdAc/U-235}} \leqslant 0{,}1$$

Vu la courte période du RdAc, ce résultat suggère qu'un des intermédiaires à vie longue: Actinium ou protactinium est précipité. Cette question sera discutée plus longuement dans un autre article.

3. Balance Géochimique des Radio-éléments dans l'Océan

Il nous a paru intéressant de recalculer la balance géochimique des éléments radioactifs dans l'océan (Koczy, 1954; Holland et Kulp, 1954) avec les valeurs expérimentales que nous avons trouvées pour Io, Th et RdTh. Nous supposons que la concentration des éléments radioactifs dans l'océan varie très lentement au cours du temps, par exemple qu'elle est pratiquement constante pendant une période de 1.000 ans. Dans ce cas, la quantité d'un radio-élément apportée ou produite dans l'océan doit être égale à la quantité retirée de l'océan. Les valeurs de production et de précipitation sont calculées par ml d'eau de l'océan et par m^2 du fond (supposant une profondeur moyenne de 4.000 mètres), l'année est prise comme unité de temps. Nous prenons β, l'apport d'eau des rivières, égal à $2 \cdot 10^{-5}$ ml par ml d'eau océanique et par an.

Ionium

La balance pour l'ionium s'écrit:

$$\lambda_{Io} \cdot Io_2 + S_{Io} = Io_0 \cdot \beta + \lambda_u \cdot U_o$$

Les quatre termes représentent successivement: la perte d'Io par désintégration radioactive, la perte d'Io par précipitation avec les sédiments, l'apport d'Io par les rivières et la production d'Io dans l'océan par désintégration de l'uranium.

Le premier terme est négligeable. En prenant les concentrations en ionium de Isaac et Picciotto (1953) pour des sédiments du Pacifique et les vitesses moyennes de sédimentation calculées par Kröll (1954) pour les mêmes sédiments, on trouve que S_{Io} est de l'ordre de $2 \cdot 10^{-9}$ g Io/m^2-a. En calculant la quantité d'ionium produite par an par l'uranium contenu dans une colonne de un m^2 et 4.000 m de haut, on trouve une valeur du même ordre.

Comme l'incertitude sur ces valeurs est de plus de 20%, on ne peut en calculer l'apport d'ionium par les rivières, mais on peut estimer d'après la concentration en Io dans l'océan que la concentration dans l'eau des rivières doit être de l'ordre de 10^{-15} à 10^{-16} g Io/ml.

Radium

$$\lambda_{Ra} \cdot Ra_0 + S_{Ra} = Ra_r \cdot \beta + \lambda_{Io} \cdot Io_0$$

Le second membre de l'équation représente seulement 10% de $\lambda_{Ra} \cdot Ra_0$. On arrive à l'intéressant résultat que S_{Ra} est négatif c'est à-dire qu'une partie du radium des sédiments (produit par la désintégration de l'ionium) doit repasser en solution dans l'océan. Le taux de dissolution est estimé à $1{,}3 \cdot 10^{-10}$ g Ra/m² — a.

Comme la vie moyenne du radium est relativement courte, on peut s'attendre à des fluctuations de cette valeur en un temps de quelques milliers d'années. Si on considère les argiles du Pacifique, la concentration en ionium dans les couches superficielles est de l'ordre de $4 \cdot 10^{-9}$ g Io/g, produisant $3{,}6 \cdot 10^{-14}$ g Ra par an. La production totale de radium dans 3.000 g de sédiment par m² devrait diffuser dans l'océan pour équilibrer l'équation du radium. Cette quantité de sédiment serait déposée en 10.000 ans et formerait une couche de l'ordre d'un cm d'épaisseur seulement. En fait, une couche plus épaisse peut contribuer si une partie seulement du radium produit repasse en solution. La distribution du radium dans les premiers centimètres des couches de sédiment serait déterminée par un équilibre dynamique entre la production par désintégration de l'ionium et la perte par diffusion dans l'océan. L'augmentation de la concentration du Radium dans les couches supérieures serait plus lente qu'on ne l'attendrait d'après les conditions de mise en équilibre avec l'ionium.

Un grand nombre de mesures de radium et d'ionium sur les sédiments et sur l'eau seront encore nécessaires pour établir la validité de cette hypothèse de la redissolution du radium des sédiments.

Thorium

L'équation pour Th-232 s'écrit

$$\lambda_{Th} \cdot Th_0 + S_{Th} = Th_r \cdot \beta$$

Le terme dû à la décroissance du thorium est négligeable.

On peut calculer une valeur maximum de S_{Th} d'après la concentration en thorium des sédiments et la vitesse de sédimentation (voir ionium). On en tire une concentration du thorium dans les rivières de $2{,}5 \cdot 10^{-11}$ g Th/ml. Il est probable qu'une partie seulement du thorium des argiles pélagiques est précipitée chimiquement de l'océan, par conséquent cette valeur est une limite supérieure de la concentration du thorium en solution dans les rivières.

Radiothorium

$$\lambda_{RdTh} \cdot RdTh_0 + S_{RdTh} = RdTh_r \cdot \beta + \lambda_{MsTh} \cdot MsTh_0$$

Comme on suppose des conditions stationnaires, $RdTh_0$ et S_{RdTh} sont constants, leur rapport est aussi constant et l'équation peut s'écrire, en négligeant l'apport du RdTh par les rivières.

$$\lambda_{MsTh} \cdot MsTh_0 = RdTh_0 (\lambda_{RdTh} + p)$$

p est la fraction de RdTh précipité par an à partir d'un ml d'eau de mer. Le terme $(\lambda + p)$ représente la perte totale en RdTh par an et par ml de l'océan.

On peut supposer que p est le même pour le radiothorium et l'ionium qui sont deux isotopes produits probablement tous deux dans les mêmes conditions (par désintégration de leur parent en solution dans l'eau de mer).

Pour l'ionium, le taux de précipitation a été déterminé égal à $3 \cdot 10^{-19}$ g Io/ml—an et la concentration dans l'océan inférieure à 10^{-16} g/ml, ce qui donne $p < 3 \cdot 10^{-3}$.

D'autre part, p ne peut être beaucoup plus grand que 0,01 d'après le fait qu'on ne trouve pas de thorium dans l'eau de mer, mais qu'on y trouve du radiothorium, ce dernier a donc un taux de production supérieur à son taux de précipitation. La concentration du Th-232 dans l'océan doit être supérieure à celle des autres isotopes du thorium et c'est elle qui détermine le taux de précipitation p. Par analogie avec la définition de la vie moyenne d'un élément radioactif, la durée de vie moyenne d'un atome de thorium dans l'océan est donnée par $1/(\lambda + p)$ comme étant inférieure à 300 ans.

Mésothorium

$$\lambda_{\mathrm{MsTh}} \cdot \mathrm{MsTh}_0 + S_{\mathrm{MsTh}} = \mathrm{MsTh}_r \cdot \beta + \mathrm{Th}_0 \cdot \lambda_{\mathrm{Th}}$$

Le membre de droite de l'équation est petit par rapport au terme $\lambda_{\mathrm{MsTh}} \cdot \mathrm{MsTh}_0$, S_{MsTh} doit être négatif. La situation du MsTh semble être analogue à celle de son isotope, le radium. La valeur de S_{MsTh} calculée est de l'ordre de 10^{-21} g MsTh/ml a, soit $4 \cdot 10^{-12}$ g/m^2—a repassent en solution dans l'océan.

Vu la courte vie du MsTh ($T = 6{,}7$ ans), on doit s'attendre à ne plus trouver de mésothorium loin des côtes et du fond de l'océan.

L'existence dans l'eau de mer de radium ($T = 1.600$ ans) et de mésothorium ($T = 6{,}7$ ans) non supportés par leur parent à vie longue offre un intérêt considérable pour l'étude de la diffusion dans l'océan et de la circulation océanique. Cette méthode complèterait les renseignements qu'on peut obtenir à ce sujet par la distribution du C-14 ($T = 6.000$ ans) et du tritium ($T = 11$ ans).

Le mésothorium, vu sa vie courte, devrait disparaître à une distance relativement petite du fond et pourrait être utilisé pour identifier des masses d'eau ayant été en contact récent avec les sédiments et pour mesurer les vitesses de courants horizontaux quittant la plate-forme continentale ou passant au voisinage de surélévations du fond de l'océan.

Remerciements—Nous remercions vivement l'Office Suédois des Pècheries qui a mis à notre disposition pour ce travail, son bateau de recherche, le "Skagerak" et le laboratoire de la station hydrographique de Bornö.

Nous tenons à témoigner notre gratitude aux Professeurs H. Pettersson (Göteborg) et F. G. Houtermans (Berne) de leurs suggestions et de l'intérêt qu'ils ont porté à ce travail.

Nous remercions enfin Mme J. Meesters, microscopiste au Laboratoire de Physique Nucléaire, pour sa collaboration.

Nous avons bénéficié, pour ce travail, de subsides de la Geological Society of America et de l'Institut Interuniversitaire Belge des Sciences Nucléaires.

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Data of rock analyses—III

New Zealand periodical and serial literature. Bibliography and index of rock analyses*

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New Zealand is probably as remarkable from a geological as from a physiographic standpoint. The variety of rocks, the range of periods represented in the strata, and the irregularity and intricacy of their structure, present many problems of interest and give to the geologist ample scope for investigation. . . .
James MacIntosh Bell
The Wilds of Maoriland.

Part III of the series on rock analysis data is concerned with New Zealand. It comprises a list of periodical and serial literature published in New Zealand, a bibliography of seventy-eight references from these publications in which chemical analyses of igneous and/or metamorphic rocks appear, and an index by rock names to the analyses given in the references. Thus Part III follows the pattern set by Parts I and II, but with one omission. No geographic index is given because, with two exceptions, the references contain only analyses of New Zealand rocks. These are Bartrum (1927), four analyses of rocks from Samoa, and Marshall (1915), three analyses of rocks from Tahiti. It might be well to repeat here that, to the best of our knowledge, only new or previously unpublished analyses are being cited in these bibliographies, and references containing only analyses known to be quoted from other publications are not included.

We wish to offer a personal word of appreciation to the staff of the New Zealand Geological Survey for their assistance as reviewers and critics of the completed manuscript.

It will be our custom, as succeeding parts of the series appear, to list those parts that have been published.

Part I. African periodical and serial literature, by Marjorie Hooker, *Geochimica et Cosmochimica Acta* **9,** nos. 1–2, 90–97 (February, 1956).

Part II. Bibliography and index of rock analyses in the African periodical and serial literature, by Marjorie Hooker, *Geochimica et Cosmochimica Acta* **9,** no. 4, 190–213 (April, 1956); Supplement, **11,** nos. 1/2, 138.

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Bartrum, John A. (1927) Igneous rocks from western Samoa: N.Z. Inst. Tr. **57,** 254–264. *Samoa:* 4; picrite basalt, olivine basalt, anorthoclase trachyte.

Bartrum, John A., and Francis J. Turner, (1928) Pillow-lavas, peridotites and associated rocks of northernmost New Zealand: N.Z. Inst. Tr. **59,** pt. 1, 98–138. 3; dolerite, gabbro, basalt.

Bartrum, John A. (1929) Igneous rocks at Mount Camel, Hohoura, North Auckland: N.Z. J. Sci. & Tech. **10,** no. 6, 356–360. 2 granophyre, andesite.

Bartrum, John A. (1936) Notes on the geology of Three Kings and other outlying islands of northern New Zealand: N.Z. J. Sci. & Tech. **18,** no. 6, 520–530. 1 rhyolite breccia.

Benson, William N., and John A. Bartrum, (1935) The geology of the region about Preservation and Chalky Inlets, south-west Fiordland, N.Z.: Roy. Soc. N.Z. Tr. **65,** pt. 2, 108–152. 3; granodiorite-aplite, slate.

Benson, William N., and Francis J. Turner, (1939a) Mineralogical notes from the University of Otago, New Zealand; No. 2. Comparative composition-variation diagrams for the Cainozoic igneous rocks of New Zealand with determinations of the optic axial angles of the pyroxenes and olivines contained therein: Roy. Soc. N.Z. Tr. **69,** pt. 1, 56–72. 5; olivine dolerite, trachybasalt, trachyandesite, kaiwekite.

Benson, William N. (1939b) Mineralogical notes from the University of Otago, N.Z.; No. 3. Kaersutite and other brown amphiboles in the Cainozoic igneous rocks of the Dunedin district: Roy. Soc. N.Z. Tr. **69,** pt. 3, 283–308. 2; trachyandesite, nepheline syenite porphyry.

Benson, William N., and Francis J. Turner (1940) Mugearites in the Dunedin district: Roy. Soc. N.Z. Tr. **70,** pt. 3, 188–199. 1 mugearite.

Benson, William N. (1942) The basic igneous rocks of eastern Otago and their tectonic environment, Part II: Roy. Soc. N.Z. Tr. **72,** pt. 1, 85–118. 10; mugearite, atlantite, basanite, olivine theralite, olivine nephelinite, limburgite.

Benson, William N. (1944) The basic igneous rocks of eastern Otago and their tectonic environment, Part IV. The mid-Tertiary basalts, tholeiites and dolerites of north-eastern Otago: Roy. Soc. N.Z. Tr. **74,** pt. 1, 71–123. 5; pillow lava, olivine dolerite, olivine basalt, pegmatoid dolerite.

Benson, William N. (1946) The basic igneous rocks of eastern Otago and their tectonic environment, Part 5. The quartz porphyry of the Shag Valley and its relation to the mid-Tertiary basaltic magma of north-east Otago; a petrogenetic essay: Roy. Soc. N.Z. Tr. **76,** pt. 1, 1–36. 2 quartz porphyry.

Berry, J. Allan (1929) The volcanic deposits of Scinde Island, with special reference to the pumice bodies called chalazoidites: N.Z. Inst. Tr. **59,** pt. 3, 571–608. 5 pumice.

Broadgate, F. K. (1916) The "red rocks" and associated beds of Wellington Peninsula: N.Z. Inst. Tr. **48,** 76–86. 1 diabase tuff.

Brown, David A. (1942) Geology of the west coast of the Firth of Thames: Roy. Soc. N.Z. Tr. **72,** pt. 1, 69–84. 1 hypersthene andesite.

Cox, P. T. (1926) Geology of the Rakaia Gorge district: N.Z. Inst. Tr. **56,** 91–111. 3; rhyolite, pitchstone, andesite.

Ferrar, Hartley T., and others (1925) The geology of the Whangarei-Bay of Islands subdivision, Kaipara Division: N.Z. Geol. Survey B. **27,** 134 p. 32; granodiorite porphyry, dacite, quartz porphyrite, porphyrite, quartz andesite, garnet-bearing andesite, hypersthene andesite, hornblende andesite, hornblende-biotite andesite, pyroxene andesite, pyroxene-hornblende andesite, olivine andesite, basalt, olivine basalt.

Ferrar, Hartley T. (1929) The soils of irrigation areas in Otago Central: N.Z. Geol. Survey B. **33,** 42 p. 2; basalt, quartz-feldspar schist.

Ferrar, Hartley T. (1934) The geology of the Dargaville-Rodney subdivision, Hokianga and Kaipara Divisions: N.Z. Geol. Survey B. **34,** 86 p. 20; andesite, hornblende andesite, dacite, rhyolite, basalt, dolerite, quartz dolerite, quartz porphyrite, granophyre, olivine basalt, olivine gabbro, teschenite, serpentine.

Gage, Maxwell (1940) The geology of the iron-ores of the Collingwood district, north-west Nelson: N.Z. J. Sci. & Tech., sec. B, **21,** no. 6, 304–313. 1 diabase.

Grange, Leslie I. (1921) An account of the geology of Green Island coalfield: N.Z. Inst. Tr. **53,** 157–174. 4; basalt, dolerite, trachydolerite.

Grange, Leslie I. (1927a) The geology of the Tongaporutu-Ohura subdivision, Taranaki Division: N.Z. Geol. Survey B. **31,** 63 p. 3; pumice, pumice sand, rhyolite tuff.

Grange, Leslie I. (1927b) On the "rodingite" of Nelson: N.Z. Inst. Tr. **58,** 160–166. 6; gabbro, grossularite-diopside rock.

Grange, Leslie I. (1929) A classification of soils of Rotorua County: N.Z. J. Sci. & Tech. **11,** no. 4, 219–228. 3 rhyolite pumice.

Grange, Leslie I. (1937) The geology of the Rotorua-Taupo subdivision, Rotorua and Kaimanawa Divisions: N.Z. Geol. Survey B. **37,** 138 p. 18; ignimbrite, rhyolite, hornblende rhyolite, andesite, dacite, basalt, obsidian, opalized andesite, rhyolite breccia.

Henderson, John (1917) The geology and mineral resources of the Reefton subdivision, Westport and North Westland Divisions: N.Z. Geol. Survey B. **18,** 232 p. 5; diabase, epidiorite, metasomatic country rock.

Henderson, John (1918) Marble in Riwaka-Takaka district: N.Z. J. Sci. & Tech. **1,** no. 3, 175–177. 1 norite.

Henderson, John (1920a) Geological features disclosed by excavations at the proposed dam site at Arapuni, Waikato River: N.Z. J. Sci. & Tech. **3,** no. 4, 224–226. 4 tuff.

Henderson, John, and Montague Ongley (1920b) The geology of the Gisborne and Whatatutu subdivisions, Raukumara Division: N.Z. Geol. Survey B. **21,** 88 p. 2 pumice.

Henderson, John, and Montague Ongley (1923a) The geology of the Mokau subdivision, with an account of adjoining areas, and of the Te Kuiti district, Pirongia and Taranaki Divisions: N.Z. Geol. Survey B. **24,** 83 p. 3; andesite, rhyolite breccia, serpentine.

Henderson, John (1923b) Notes to accompany a geological sketch-map of the Mount Arthur district: N.Z. J. Sci. & Tech. **6,** no. 3, 174–190. 4; basalt, gabbro, pyroxenite, grossularite rock.

Henderson, John, and Leslie I. Grange (1926) The geology of the Huntly-Kawhia subdivision, Pirongia and Hauraki Divisions: N.Z. Geol. Survey B. **28,** 112 p. 16; andesite, hornblende-augite andesite, augite-olivine andesite, basalt.

Henderson, John (1935) Notes on the geology of the Marlborough goldfields: N.Z. Geol. Survey, 29th Ann. Rpt., 11–21. 3 chlorite-, sericite-, quartz-feldspar schist.

Henderson, John (1950) Cornish stone and feldspar in New Zealand: N.Z. J. Sci. & Tech., sec. B, **31,** no. 6, 25–44. 4; aplite, granite, granodiorite porphyry.

Hutton, C. Osborne (1940) Metamorphism in the Lake Wakatipu region, western Otago, New Zealand: N.Z. Dept. Sci. Ind. Res., Geol. Mem. **5,** 84 p. 11 quartz-, chlorite-, actinolite-, ferruginous, manganiferous schist.

Hutton, C. Osborne (1942) Fuchsite-bearing schists from Dead Horse Creek, Lake Wakatipu region, western Otago: Roy. Soc. N.Z. Tr. **72,** pt. 1, 53–68. 2 fuchsite schist.

Hutton, C. Osborne (1943a) The igneous rocks of the Brocken Range-Ngahape area, eastern Wellington: Roy. Soc. N.Z. Tr. **72,** pt. 4, 353–370. 6; albite dolerite, quartz-albite dolerite, olivine dolerite, teschenite, variolite.

Hutton, C. Osborne (1943b) Limburgite from Nevis Bluff, Kawarau Gorge, central Otago: Roy. Soc. N.Z. Tr. **73,** pt. 1, 58–67. 1 limburgite.

Hutton, C. Osborne (1944) Some igneous rocks from the New Plymouth area: Roy. Soc. N.Z. Tr. **74,** pt. 2, 125–153. 3; dacite, basified dacite, porphyrite.

Maclaurin, J. S. (1916) Laboratory report, 1915: N.Z. Dom. Lab., 49th Ann. Rpt., 55 p. 1 gabbro.

Marshall, Patrick (1915) The geology of Tahiti: N.Z. Inst. Tr. **47,** 361–376. *Tahiti:* 3; limburgite, syenite, wehrlite.

Marshall, Patrick (1918) The geology of the Tuapeka district, central Otago Division: N.Z. Geol. Survey B. **19,** 79 p. 1 nephelinite basanite.

Marshall, Patrick (1928) A natrolite tinguaite from Dunedin: N.Z. Inst. Tr. **58,** 533–535. 1 natrolite tinguaite.

Marshall, Patrick (1935) Acid rocks of the Taupo-Rotorua volcanic district: Roy. Soc. N.Z. Tr. **64,** pt. 3, 323–366. 1 tridymite rhyolite.

Marshall, Patrick (1936) The mineral tuhualite: Roy. Soc. N.Z. Tr. **66,** pt. 3, 330–336. 4 comendite.

Marshall, Patrick (1946) Zeolite minerals as original components of igneous rocks: N.Z. J. Sci. & Tech., sec. B, **28,** no. 1, 37–52. 1 natrolite tinguaite.

Mason, Brian (1949) The geology of Mandamus-Pahau district, north Canterbury: Roy. Soc. N.Z. Tr. **77,** pt. 3, 403–428. 1 olivine basalt.

Mason, Brian (1951) The syenite and associated rocks of the Mandamus-Pahau area, north Canterbury, New Zealand: Roy. Soc. N.Z. Tr. **79,** pt. 2, 260–275. 5; syenite, olivine gabbro, trachyte, sodalite phonolite, trachytic matrix of igneous breccia.

Morgan, Percy G.. and John A. Bartrum (1915) The geology and mineral resources of the Buller-Mokihinui subdivision, Westport Division: N.Z. Geol. Survey B. **17,** 210 p. 3 hornfels.

Morgan, Percy G. (1924) The geology and mines of the Waihi district, Hauraki goldfield, New Zealand: N.Z. Geol. Survey B. **26,** 218 p. 17; quartz andesite, hornblende-hypersthene andesite, hypersthene andesite, andesite, dacite, tridymite rhyolite, rhyolite-tuff.

Morgan, Percy G., and Walcot Gibson (1927) The geology of the Egmont subdivision, Taranaki: N.Z. Geol. Survey B. **29,** 99 p. 14; andesite, augite-andesite, hornblende-andesite, volcanic conglomerate.

Ongley, Montague, and Eric O. McPherson (1928) The geology of the Waiapu subdivision, Raukumara Division: N.Z. Geol. Survey B. **30,** 79 p. 12; basalt, basalt porphyry, dolerite, gabbro, trachyte, tuff.

Park, James (1918) The geology of the Oamaru district, north Otago (Eastern Otago Division): N.Z. Geol. Survey B. **20,** 124 p. 1 quartz-feldspar schist.

Park, James (1919) On the occurrence of three bands of marble at South Peak, near Hampden, Otago: N.Z. Inst. Tr. **51,** 41–42. 1 marble.

Park, James (1921) Geology and mineral resources of western Southland: N.Z. Geol. Survey B. **23,** 88 p. 4; hornblende diorite, quartz-biotite diorite, aplite, gabbro.

Park, James (1926) Granite enclosures in a quartz-biotite-diorite at Green Islets, Southland: N.Z. Inst. Tr. **56,** 384–386. 3; aplite, diorite, granite.

Reed, John J. (1950) Spilites, serpentinites and associated rocks of the Mossburn district, Southland: Roy. Soc. N.Z. Tr. **78,** pt. 1, 106–126. 1 spilite.

Reed, John J. (1951) Hornblende andesite rocks from Solander Island: Roy. Soc. N.Z. Tr. **79,** pt. 1, 119–125. 1 hornblende andesite.

Searle, E. J. (1944) Geology of the southern Waitakere Hills region west of Auckland City: Roy. Soc. N.Z. Tr. **74,** pt. 1, 49–70. 1 pillow lava.

Service, Harold (1937) An intrusion of norite and its accompanying contact metamorphism at Bluff, New Zealand: Roy. Soc. N.Z. Tr. **67,** pt. 2, 185–217. 17; hornblende schist, granulite, metadolerite, epidiorite, spilitic tuff, quartz keratophyre, hornfels, norite, quartz diorite, granite.

Speight, Robert (1922) The rhyolites of Banks Peninsula: Canterbury Mus. Rec. **2,** no. 2, 77–89. 5; rhyolite, pitchstone.

Speight, Robert (1923) The intrusive rocks of Banks Peninsula: Canterbury Mus. Rec. **2,** no. 3, 121–150. 20; basalt, hornblende basalt, syenite, gabbro, trachyte, tridymite trachyte, trachyandesite, olivine trachyandesite, contact rock.

Speight, Robert (1924) The basic volcanic rocks of Banks Peninsula: Canterbury Mus. Rec. **2,** no. 4, 239–267. 6; oligoclase andesite, olivine andesite, basalt.

Speight, Robert (1928a) The geology of the Malvern Hills: N.Z. Dept. Sci. Ind. Res., Geol. Mem. **1,** 72 p. 11; andesite, dolerite, basalt, rhyolite, pitchstone.

Speight, Robert (1928b) The geology of View Hill and neighbourhood: N.Z. Inst. Tr. **58,** 408–431. 5; basalt (pillow lava), dolerite, hypersthene dolerite.

Speight, Robert (1935) The geology of Gebbies Pass, Banks Peninsula: Roy. Soc. N.Z. Tr. **65,** pt. 3, 305–328. 6; andesite, dolerite, rhyolite.

Speight, Robert (1938a) The dykes of the Summit Road, Lyttelton: Roy. Soc. N.Z. Tr. **68,** pt. 1, 82–99. 7; andesite, basalt, dolerite, trachyte, soda trachyandesite.

Speight, Robert (1938b) The geology of the Mount Somers district: N.Z. Dept. Sci. Ind. Res., Geol. Mem. **3,** 96 p. 12; andesite, garnet-hypersthene andesite, dolerite, rhyolite, rhyolite tuff, pitchstone, basic glass.

Speight, Robert (1940) The basal beds of the Akaroa Volcano: Roy. Soc. N.Z. Tr. **70,** pt. 1, 60–76. 7; andesite, dolerite, trachyte, trachyte tuff, trachyte porphyry, gabbro, contact rock.

Speight, Robert (1944) The geology of Banks Peninsula, a revision; Part II. The Akaroa Volcano: Roy. Soc. N.Z. Tr. **74,** pt. 3, 232–254. 8; andesite, basalt, soda trachyte.

Taylor, B. L. (1943) Decomposed granite, Baton, Nelson: N.Z. J. Sci. & Tech. sec. B, **25,** no. 2, 78–86. 1 granite.

Taylor, Norman H. (1930) The relation of geology to sheep sickness in Mairoa district: N.Z. J. Sci. & Tech. **12,** no. 1, 1–10. 4; andesite ash, rhyolite ash.

Turner, Francis J. (1939) Hornblende-gneisses, marbles and associated rocks from Doubtful Sound, Fiordland, New Zealand: Roy. Soc. N.Z. Tr. **68,** pt. 4, 570–598. 9; gneiss, amphibolite.

Uttley, G. H. (1918) The volcanic rocks of Oamaru, with special reference to their position in the stratigraphic series: N.Z. Inst. Tr. **50,** 106–117. 2 pillow lava.

Wellman, H. W. (1942) Talc-magnesite and quartz-magnesite rock, Cobb-Takaka district: N.Z. J. Sci. & Tech., sec. B, **24,** no. 3, 103–127. 5 serpentine.

Williamson, John H. (1939) The geology of the Naseby subdivision, central Otago: N.Z. Geol. Survey B, **39,** 141 p. 23; basalt, quartz-feldspar schist.

Rock Name Index

Amphibolite	Turner 1939
Andesite	Bartrum 1929; Cox 1926; Ferrar 1934; Grange 1937; Henderson 1923a, 1926; Morgan 1924, 1927; Searle 1944; Speight 1928a, 1935, 1938a, 1938b, 1940, 1944
augite	Morgan 1927
augite-hornblende	Morgan 1927
augite-olivine	Henderson 1926
garnet	Ferrar 1925
garnet-hypersthene	Speight 1938b

Andesite—*contd.*	
hornblende	Ferrar 1925, 1934; Morgan 1927; Reed 1951
hornblende-augite	Henderson 1926; Morgan 1927
hornblende-biotite	Ferrar 1925
hornblende-hypersthene	Morgan 1924
hypersthene	Brown 1942; Ferrar 1925; Morgan 1924
oligoclase	Speight 1924
olivine	Ferrar 1925; Speight 1924
opalized	Grange 1937
pyroxene	Ferrar 1925
pyroxene-hornblende	Ferrar 1925
quartz	Ferrar 1925; Morgan 1924
Andesite ash	Taylor 1930
Aplite	Henderson 1950; Park 1921, 1926
Ash	
andesite	Taylor 1930
rhyolite	Taylor 1930
volcanic	Allen 1948
Atlantite	
biotite	Benson 1942
zeolitized	Benson 1942
Basalt	Bartrum 1928; Ferrar 1929, 1934; Grange 1921, 1937; Henderson 1923b, 1926; Ongley 1928; Speight 1923, 1924, 1928a, 1928b, 1938a, 1944; Williamson 1939
andesitic	Ferrar 1925
hornblende	Speight 1923
olivine	Bartrum 1927; Benson 1944; Ferrar 1925, 1934; Mason 1949
Basanite, zeolitized	Benson 1942
Comendite	Marshall 1936
Conglomerate, volcanic	Morgan 1927
Dacite	Ferrar 1934; Grange 1937; Hutton 1944; Morgan 1924
andesitic	Ferrar 1925
basic	Hutton 1944
trachytic	Ferrar 1925
Diabase	Gage 1940; Henderson 1917
Diorite	Park 1926
hornblende	Park 1921
quartz	Service 1937
quartz-biotite	Park 1921
Dolerite	Bartrum 1928; Ferrar 1934, Grange 1921; Ongley 1928; Speight 1928a, 1928b, 1935, 1938a, 1938b, 1940
albite	Hutton 1943a
albite-meta-	Service 1937
hypersthene	Speight 1928b
pegmatoid	Benson 1944
olivine	Benson 1939a, 1944; Hutton 1943a
quartz	Ferrar 1934
quartz-albite	Hutton 1943a
Epidiorite	Henderson 1917; Service 1937
Gabbro	Grange 1927b, Henderson 1923b, Maclaurin 1916; Ongley 1928; Park 1921; Speight 1923, 1940
noritic	Bartrum 1928
olivine	Ferrar 1934; Mason 1951

Glass, basic	Speight 1938b
Gneiss	Turner 1939
Granite	Henderson 1950; Park 1926; Service 1937; Taylor 1943
Granodiorite-aplite	Benson 1935
Granophyre	Bartrum 1929; Ferrar 1934
Granulite (aplite)	Park 1921; Service 1937
Grossularite rock	Henderson 1923b
Grossularite-diopside rock	Grange 1927b
Hornfels	Morgan 1915; Service 1937
Ignimbrite	Grange 1937
Kaiwekite	Benson 1939a
Keratophyre, quartz	Service 1937
Lava, pillow	Benson 1944; Searle 1944; Speight 1928b; Uttley 1918
Limburgite	Allen 1951; Benson 1942; Hutton 1943b; Marshall 1915
Marble	Park 1919
Miscellaneous	
Contact rock	Speight 1923, 1940
Country rock, metasomatic	Henderson 1917
Mugearite	Benson 1940, 1942
Nephelinite, olivine	Benson 1942
Nephelinite-basanite	Marshall 1918
Norite	Henderson 1918; Service 1937
hornblende	Service 1937
olivine	Service 1937
quartz	Bartrum 1920
Obsidian	Grange 1937
Phonolite, sodalite	Mason 1951
Picrite-basalt	Bartrum 1927
Pitchstone	Cox 1926; Speight 1922, 1928a, 1938b
Porphyrite	Hutton 1944
quartz	Ferrar 1925, 1934
Porphyry	
basalt	Ongley 1928
granodiorite	Ferrar 1925; Henderson 1950
nepheline-syenite	Benson 1939b
quartz	Benson 1946
trachyte	Speight 1940
Pumice	Berry 1928; Grange 1927a; Henderson 1920b
rhyolite	Grange 1929
Pumice sand	Grange 1927a
Pyroxenite	Henderson 1923b
Rhyolite	Cox 1926; Ferrar 1934; Grange 1937; Speight 1922, 1928a, 1935, 1938b
hornblende	Grange 1937
tridymite	Marshall 1935; Morgan 1924
Rhyolite ash	Taylor 1930
Rhyolite breccia	Bartrum 1936; Grange 1937; Henderson 1923a
Schist	
actinolite	Hutton 1940
chlorite	Hutton 1940
ferruginous and manganiferous	Hutton 1940
fuchsite	Hutton 1942

Schist—*contd.*	
hornblende	Service 1937
sericite	Henderson 1935
quartz	Hutton 1940
quartz-feldspar	Ferrar 1929; Henderson 1935; Park 1918; Williamson 1939
Serpentine	Ferrar 1934; Henderson 1923a; Wellman 1942
Slate	Benson 1935
Spilite	Reed 1950
Syenite	Marshall 1915; Mason 1951; Speight 1923
Teschenite	Ferrar 1934; Hutton 1943a
Theralite, olivine	Benson 1942
Tinguaite, natrolite	Marshall 1928, 1946
Trachyandesite	Benson 1939a; Speight 1923
olivine	Speight 1923
phonolitic	Benson 1939a, 1939b
soda	Speight 1938a
Trachybasalt	Benson 1939a
Trachydolerite	Grange 1921
Trachyte	Mason 1951; Ongley 1928; Speight 1923, 1938a, 1940
anorthoclase	Bartrum 1927
soda	Speight 1944
tridymite	Speight 1923
Trachytic matrix, igneous breccia	Mason 1951
Tuff	Henderson 1920; Ongley 1928
diabase	Broadgate 1916
rhyolitic	Grange 1927a; Morgan 1924; Speight 1938b
spilitic	Service 1937
trachyte	Speight 1940
Variolite	Hutton 1943a
Wehrlite	Marshall 1915

Data of rock analyses—II (Supplement)

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Due to the inevitable lag between publication and distribution of literature, the following references were not included in Part II which appeared in volume 9, no. 4, 190–213 (April 1956).

Agard, Jules, and François Permingeat (1952) Etain, wolfram et molybdène: Morocco, Serv. Géol. Notes et Mém. **87,** 17–44. *Morocco*: 2 granite.

Agard, Jules, Jacques Destombes, and A. Jeannette (1953) Les gisements de vermiculite du Haut Atlas de Midelt: Morocco, Serv. Géol. Notes et Mém. **117,** 275–287. *Morocco*: 2; gabbro, plagioclasite.

Choubert, Georges, Henri Termier, and Geneviève Termier (1951) Les calcaires précambriens de Taghdout et leurs organismes problématiques: Morocco, Serv. Géol. Notes et Mém. **85,** 9–34. *Morocco*: 1 hornfels.

Jérémine, Elisabeth (1951) Sur une météorite (chondrite) tombée au Maroc le 22 Août 1932: Morocco, Serv. Géol. Notes et Mém. **85,** 201–208. *Morocco*: 1 meteorite.

Jérémine, Elisabeth (1952) Sur les gabbros et quelques roches associeés du Haut Atlas (feuilles de Midelt, de Kasba Tadla et d'Ouaouizarhte): Morocco, Serv. Géol. Notes et Mém. **95,** 215–235. *Morocco*: 3; harrisite, olivine gabbro, syenite.

Jouravsky, Georges (1952) Cobalt et nickel: Morocco, Serv. Géol. Notes et Mém. **87,** 87–101. *Morocco*: 1 serpentine.

Shukri, Nasri M. (1953) The geology of the desert east of Cairo: Inst. Desert Egypte Bull. **3,** 89–105. *Egypt*: 1 basalt.

GEOCHEMICAL NOTE

The determination of rubidium in sea water by the stable-isotope dilution method

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THE rubidium content of sea water was determined recently by radioactivation analysis (SMALES and SALMON, 1955) and found to be 120 ± 10 μg/litre. This value, which was lower than those reported by other workers by a factor of almost 2, has now been confirmed by the stable-isotope dilution method for a sample of North Atlantic sea water (49° 02′ N, 15° 19′ W) taken from a depth of 4000 metres.

Separation of the rubidium from other salts present was not necessary. Aliquots of a solution of a rubidium tracer enriched in ^{87}Rb (^{85}Rb 15·0$_5$%; ^{87}Rb 84·9$_5$%) were mixed thoroughly with measured volumes of sea water in polythene bottles. In each case a small portion of the mixture was acidified with sulphuric acid and heated to dryness in a platinum crucible. A little of the aqueous extract of the residue was dried on the tungsten filament of a mass-spectrometer source unit, and the rubidium isotope ratio determined. The sample used for each mass spectrometric analysis contained approximately 0·01 μg of rubidium sulphate.

The results listed in Table 1 were calculated with the following formula:

$$x = y \cdot \frac{85 \,.\, R_N + 87}{85 \,.\, R_T + 87} \cdot \frac{R_M - R_T}{R_N - R_M}$$

where R_N is the $^{85}Rb/^{87}Rb$ ratio of the normal element, R_T is the $^{85}Rb/^{87}Rb$ ratio of the tracer element, R_M is the $^{85}Rb/^{87}Rb$ ratio of the mixture, y is the weight of tracer rubidium added, and x is the weight of rubidium in the sample.

The concentration of the tracer solution was determined by isotope dilution, using a standard solution of normal rubidium prepared from "Specpure" rubidium chloride.

If the uncertainty is estimated from the standard deviations of the above determination, the calibration of the tracer solution, and the measurement of the natural rubidium abundance ratio, a value of 121·4 ± 5 μg/litre is obtained for the rubidium content of sea water. This is in good agreement with the figure of 120 ± 10 μg/litre found by radioactivation analysis.

Table 1

Volume of tracer solution (2·62 μg/ml)	Volume of sea-water	R_M	Rubidium content (μg/litre)	Mean value and standard deviation
2 ml	10 ml	0·350	121·7	
2 ml	30 ml	0·629	121·0	
				121·4 ± 1·1
1 ml	20 ml	0·741	120·1	
1 ml	20 ml	0·750	122·6	

SMALES A. A. and SALMON L. (1955) *The Analyst* **80**, 37.

LETTER TO THE EDITORS

Effect of lanthanide contraction in geochemistry

(*Received* 7 *August* 1956)

K. Rankama, Th. G. Sahama: *Geochemistry*, Chicago, 1952. Chapter 5. Geochemistry of the Lithosphere (Particle Size) pp. 106–111.

While it is quite possible to interpret the effect of lanthanide contraction on the geochemical coherence of the pairs of elements Zr-Hf, Nb-Ta, Mo-W, it seems less correct to present ionic radii of elements in the form given in Table 5.7 of the above-mentioned book. It would, in fact, be more suitable to distinguish A and B groups of elements in the table as is usually done in the modern forms of the periodic table of elements.

We may take the ionic radii of the alkali metals as the unit, but when we do so the ionic radii of the copper group Cu, Ag, Au and the other groups of heavy metals can also be reduced to the alkali metals (=1). For instance—instead of Ag(1): Cd(0·81) relation we count with Rb(1): Cd (0·69) values, and naturally the Rb(1): Ag (0·76) relation too. This form shows clearly not only the effect of lanthanide contraction (*f*-contraction), but the same table will also show the influence of *d*-contraction in the group of heavy metals (*d*-contraction of elements Ta—Pt). The double-contraction effect observed at the Ag-Au pair of elements has recently been mentioned by B. Lakatos (1954). Ionic radii are not always the most suitable parameters for measuring particle sizes.

There are more factors in the periodic system of elements affecting their size, and hence it is not advisable to simplify the relations in this way, especially for the series Au—Hg—Tl—Pb—Bi. A more detailed report will be found in *Věstník* ÚÚG (in the press for 1957).

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